

Syngas to Bio-ethanol Fermentation

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Executive Summary

Minimizing waste and environmental impact of industrial installations is a relevant concern in 2018, and a modern engineer is more so than ever asked to solve environmental challenges pertaining to future and legacy technology. An area with large waste streams, and great potential for innovation is the steel industry, which produces large volumes of toxic and greenhouse gasses like carbon monoxide and carbon dioxide. Typically, said gasses are burned, but steel furnace exhaust gasses have a very low heating value, being ten times less productive than natural gas^{1 2}. A possible alternative to burning said gas is to convert it into a useful product. As early as the 1990s, publications arose discussing the conversion of synthetic gas (syngas) using the wood-ljungdahl pathway, a metabolic pathway used by anaerobic microbes to convert carbon monoxide and carbon dioxide to products like acetic acid and ethanol, among other less prominent products³. One of the first microbes studied in this fermentation process was *Clostridium ljungdahlii* (*C.ljungdahlii*)³. Despite the early discovery of the wood-Ljungdahl pathway and the possibilities *C.ljungdahlii* offered in syngas conversion, very few implementations of syngas bio-fermentation processes exist, and none at significant industrial scale. In order to assess the potential of syngas bio-fermentation in conjunction with steel gas waste streams, this paper examines the economic viability of said process by designing a syngas bio-fermentation plant using exhaust gasses of a TATA steel plant in southern Holland. This paper begins by introducing *C.ljungdahlii*, the microbe of choice, and the pathway used in the bioreactor. Next, reactor choice and design occur, followed by a syngas pretreatment design, then product purification design. The design process involves both theoretical design calculations, and process simulation using Aspen Plus. Lastly, the cost and turnover of said installation is examined to determine whether such a project is viable. Cost analysis was achieved using Aspen Plus Economic Analyzer, and process costing theory from Chemical Engineering Design by Towler and Sinnott⁵³. Our findings estimate a near \$8.64 billion-dollar project investment cost, with a \$1.8 billion-dollar turnover on ethanol sales from the plant annually, the plants primary product. The process is found to be extremely energy intensive, with the plant under steady state operation estimated to consume nearly 5.93GW. Due to the large energy demands of product purification and syngas pretreatment, the project was found to be un-economical. This approach does however offer valuable information for future designs, as expensive aspects of syngas fermentation are highlighted, such as the syngas pretreatment, which is responsible for 85% of the initial \$8.64 billion-dollar investment. With this in mind, future investigations should focus on minimizing syngas pretreatment and implementing energy saving measures to create a less energy intensive and laborious process, which may make syngas bio-fermentation profitable.

Contents

Chapter I - INTRODUCTION	6
Background	7
Steel-mill off-gases	7
Ethanol supply and demand	8
Chemical vs. biological catalysis	9
Wood-Ljungdahl pathway (WLP) based biocatalytic mechanism	11
Design Parameters	13
Objectives	13
Steel-mill off-gas stream specification	13
Biocatalyst specifications	14
Chapter II - PROCESS DESIGN	16
Reactor Design	17
Reactor criteria and design	17
Clostridium ljungdahlii	17
Previous applications	18
Reactor Choice	18
Process Upscale and Optimization	21
Syngas Optimization	27
Auxiliary Calculations	34
Syngas processing	36
Carbon based solids	36
Tar removal	37
Hydrogen sulfide removal	38
NO and SO ₂ removal	39
Nitrogen removal	40
Syngas process modeling	41
Raw gas feed	41
Cyclone	42

Compressors	43
Heat exchangers.....	43
Tar reformer.....	43
Fixed bed reactors.....	44
CSTR	45
Results	45
Reactor Model	46
Growth/acidogenesis reactor (R1)	46
Production/solventogenesis reactor (R2)	49
Product Work-up	54
Extractive distillation.....	54
Product work-up feed	55
Process design.....	56
Feed preparation	57
Feed pre-heating	62
Chapter III - CONTROL AND INSTRUMENTATION	64
Syngas processing	65
Pressure control	65
Temperature control	66
Fixed bed reactor control systems	67
pH control.....	68
Continuous stirred tank reactors	69
Storage tanks.....	70
Demister.....	70
Growth/acidogenesis reactor (R1).....	70
Acid – Base Control	71
Nutrient and Water Control	73
Syngas Out and Product Recovery Control.....	74
Liquid Out and Cooling Control.....	75
Reactor Control.....	76
Production/Solventogenesis Reactor (R2)	77
pH control system.....	78
Foaming control system.....	79
Primary metabolite steady-state concentration control system	80
Gas inlet control system and pressure loss safety measures	81

Gas inlet composition control system.....	82
Reactor pressure control system and safety measures.....	82
Reactor temperature control system	83
Reactor liquid level control system	84
Cell recycle control system.....	85
Cell filtration module control system	85
Flasher pressure and liquid storage pressure control system.....	86
Product Work-up	87
After HAZOP	88
Chapter IV - EQUIPMENT SPECIFICATION.....	90
Syngas Cleanup	91
Tar reformer.....	91
Fixed bed reactor	91
CSTR	91
Pumps	91
Tanks	92
Nitrogen Membrane filters	92
Heat exchangers.....	92
Material of Construction (MoC).....	92
Growth/acidogenesis reactor (R1).....	94
Heat Exchanger.....	96
Tanks	97
Vessels	97
Flashers	97
Pumps	98
Filtration	99
Production/solventogenesis reactor (R2)	99
Vessel(s)	99
Tank(s).....	101
Pump(s).....	102
Heat exchanger(s)	107
Filter(s)	107
Product Work-up	108
Distillation columns.....	108
Heating/cooling equipment.....	111

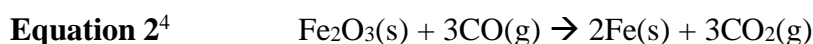
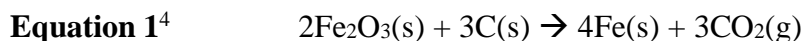
Pumps	112
Tanks	112
Chapter V - COST ANALYSIS AND CONCLUSION	114
Equipment Cost	115
Syngas processing.....	115
Growth/acidogenesis reactor (R1)	116
Production/solventogenesis reactor (R2)	116
Product Work-up	118
Capital Fixed Investment Costs.....	119
Annual product value	119
Conclusion.....	120
Bibliography	121

Chapter I - INTRODUCTION

Background

Steel-mill off-gases

In the steel industry, unlike typical industries, carbon is mainly used in the reduction process of iron oxides to form metallic iron, and not as a fuel source. This reduction follows the reactions which are shown in **Equation 1** and **Equation 2**⁴.



While alternative energy sources to replace carbon-based fuels are relatively easy to come by nowadays, such as by utilizing wind and solar energy, they are still unable to replace the functionality of the carbons being used in steel production. This implies that, regardless of the green energy movement, steel-mill waste gas is an unavoidable residue of industrial production, within the steel industry specifically.

These off-gases from the production of iron and steel, while they can vary in terms of their exact composition, would generally contain significant amounts of carbon monoxide (CO) and carbon dioxide (CO₂), as shown in **Table 1**⁵. In producing one metric ton of steel, an average of 1.8 metric tons of off-gases are emitted⁶. This results in the global iron and steel industry alone contributing approximately 5-7 percent to the worldwide CO₂ emission, which is one of the greenhouse gas (GHG)⁷. Since the reduction of GHG emissions is a pressing issue and has been identified as one of the most important challenges for current societies, new technologies to achieve large reductions in GHG emissions are of necessary. This is because up to now, most of the off-gases from steel-mills were either flared or used to create process heat and electrical energy somewhere else within the plant⁸.

Source	CO (%)	CO ₂ (%)	H ₂ (%)	N ₂ (%)	Other (%)
Basic O2 furnace	50-70	10-20	1-2	15-30	-
Blast furnace	20-35	20-30	2-4	50-60	-
Coke oven gas	5-10	3-5	55	10	25 (CH ₄)

Table 1. Typical off-gases composition from steel production⁵

Ethanol supply and demand

Ethanol is a relatively low-costing fuel alternative and is of high demand. This is reflected by its estimated market value of USD 64.52 billion in 2016, amounting to an annual volume of over 80 million metric tons. Ethanol consumption is also predicted to steadily grow in the years to come^{9,10}. Ethanol found its application mainly in vehicle fuels as it is being used to improve fuel octane, and also possesses several attractive benefits over traditional fuels like unblended gasoline. From an environmental standpoint, ethanol is much less harmful when compared to unblended gasoline as generally CO, CO₂, and oxides of nitrogen emission from an ethanol combustion process are significantly lower than that of gasoline, amounting to a reduction of GHG emission in the range of 15-65 percent, relative to gasoline, depending also on the source of ethanol¹¹. Furthermore, the use of ethanol as a fuel would also prevent harmful chemical fuel additives, such as methyl tert-butyl ether (MTBE) and benzene, to be in the air. While low percentages gasoline-ethanol blends such as blend E10 and E15 are where the majority of the current ethanol global productions are being allocated to, progress on a more complete transition to ethanol-based or ethanol-rich vehicle fuels, such as the E85 blend, is what keeps increasing the demand for this particular commodity. This, therefore, makes ethanol a commodity of economic interest in developing a chemical process.

Generally, ethanol is produced mostly from the use of renewable or bio-based raw material feedstock, such as starch, corn, and cellulose¹². This makes ethanol easy to source since it comes from corn, starch or cellulose, implying that one can now practically cultivate their own fuel, adding further a benefit of independence regarding domestic or national oil needs¹¹. One of the biggest drawbacks for such ethanol production is, however, the fact that fuel production is now in competition with food production in terms of resources. One can argue that such process would also harm the environment, albeit in a different way. Additionally, factoring in energy costs, as reported in a 2005 study by a Cornell University researcher David Pimental, the present production method of ethanol is said to have an overall energy deficit between 27-57 percent, implying that, by transitioning to ethanol, more energy would be required for its production, which would render the said process less environmentally friendly¹³.

Chemical vs. biological catalysis

As it follows from the previously stated points, it would, therefore, be highly beneficial to devise a process, able to convert the previously mentioned steel production off-gases into ethanol. Not only would it enable the recovery of carbon lost in the steel's waste gas stream, it will also be converted into a commodity of economic significance and environmental benefit.

One example of such a process could be the metal-catalyzed conversion of CO and H₂ to hydrocarbons via the well-known Fischer–Tropsch (FT) process. Invented by Franz Fischer and Hans Tropsch in 1925, the chemically catalytic process has been used to perform the conversion of gases into hydrocarbons since the 1930s at an industrial scale¹⁴. FT process work by passing a stream of gas through beds of metal catalysts, consisting of mainly transition metals, such as iron, cobalt, and ruthenium, which at high enough temperatures and pressures, will convert the CO and H₂ components of the gas stream into a mixture of liquid hydrocarbons¹⁵. This mixture of hydrocarbons will then require further processing depending on the specific target chemical at the end of the process¹⁵.

FT processes, however, have a number of disadvantages. The catalyst bed used to convert the gases in FT processes are generally highly sensitive, even to trace amounts of common gas contaminants such as sulfur species¹⁵. This, therefore, implies that in order for FT to be economically feasible, a very clean gas stream is one of the requirement for the prevention of the poisoning of catalyst bed consisting of numerous expensive and rare-earth metals. Furthermore, this is also what makes FT unsuited for the conversion of industrial off-gases, such as in the case of steel-mill. Additionally, the FT process is also known to require a specific CO: H₂ ratio in order for it to work optimally¹⁴. This further constrains the usability of said process, as it would be unlikely for the specific ratio requirement to be met by the composition of industrial off-gases.

Unlike the FT process, its biocatalytic counterpart, the fermentation of CO and CO₂ rich off-gases, often require less gas conditioning and offer more flexibility in terms of the gas composition it can handle. While the exact amount of gas pre-treatment required for fermentation-based process is also highly dependent on the nature of the contaminants and the tolerance of the specific biocatalyst being used, due to the sheer number of biocatalysts one can choose from, relative to FT, a biocatalytic pathway would still offer a higher tolerance¹⁵. Furthermore, fermentative conversion of CO and CO₂ rich gases also possess an additional selectivity benefit if compared to the FT process. While complex, biological processes tend to

be highly tunable to be highly specific regarding the product composition being formed. This is especially the case, as selective and highly efficient gene editing tools, such as CRISPR/Cas9 are extensively available for microbes¹⁶. Additionally, a biocatalytic process in general works at very mild conditions, often at atmospheric pressure and very close to room temperature, instead of requiring high operating pressure and temperature for the reactions to be carried out. Lastly, biocatalytic pathways also provide the added benefit of being generally more environmentally friendly, as it utilizes microbes rather than exotic rare-earth metals as the catalyst for the process.

Fermentation-based processes, however, are not without limitation. By production capability alone, the volumetric production rates of hydrocarbons in FT process are generally very high, which enables centralized large-scale production plants¹⁵. Biological processes on the other hand, while also highly dependent on design optimization and the specific biocatalyst being used, tend to exhibit low production rates relative to that of FT process. In this sense, a biological process simply would not be able to compete with a chemically catalytic process like FT. Furthermore, despite the required gas conditioning resulting in additional cost in the commercialization of the FT process, a biocatalytic process would often still cost more in its commercial adaptation, owing to the so-called early adopters' tax, as the said process is still early-in-development. And finally, in terms of background knowledge, chemically catalytic processes are generally much better understood and well-documented than its biocatalytic analog, owing to the generally much simpler nature of standalone or even a series of chemical reactions if being compared to a full metabolic pathway. An implication of this is that the development of a biocatalytic process would involve significantly more trial and error element due to the lack of fundamental understandings, which can therefore significantly complicate scale-up and optimization of said process.

Wood-Ljungdahl pathway (WLP) based biocatalytic mechanism

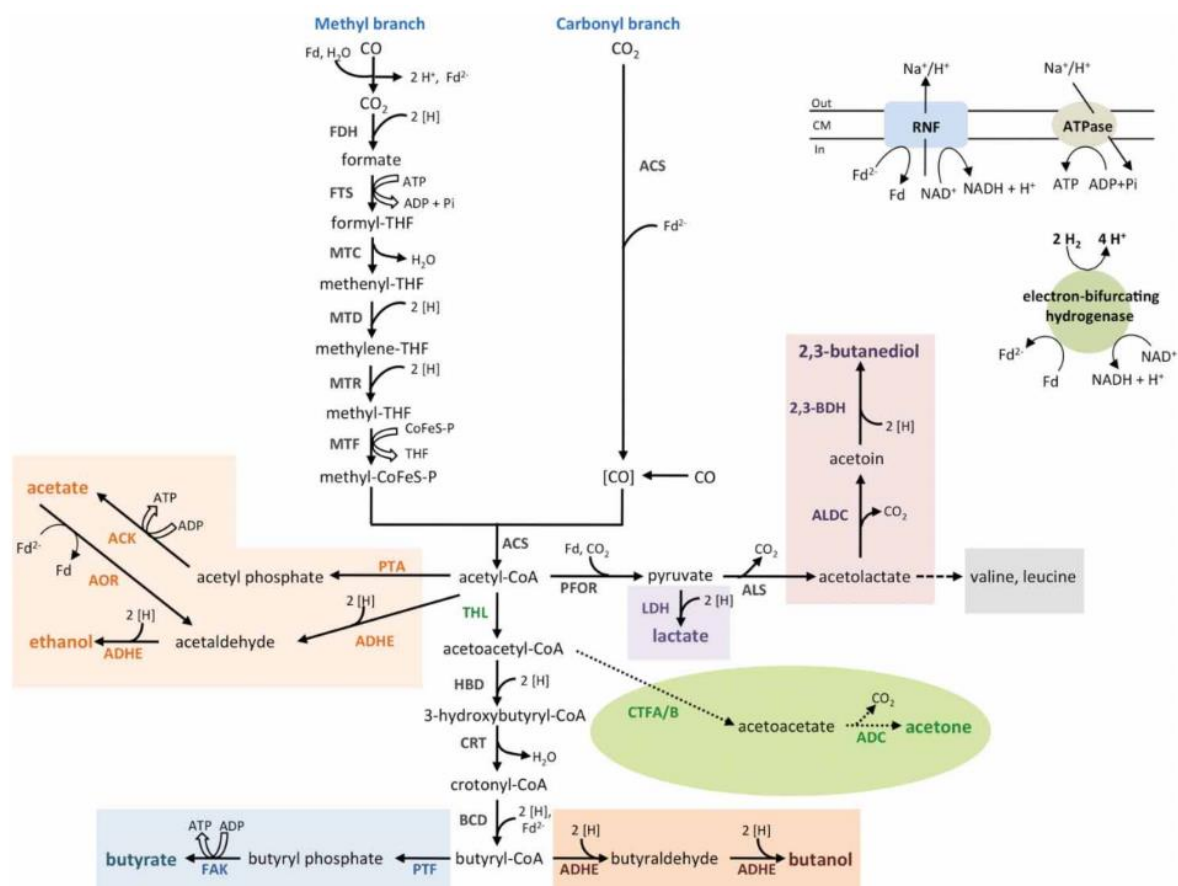


Figure 1. Wood-Ljungdahl pathway¹⁷

Syngas fermenting biocatalysts generally are able to utilize the WLP, also known as the reductive acetyl-CoA pathway as it reduces CO and also CO₂ in the presence of H₂. Syngas fermenting microbes utilize the said pathway to uptake CO, CO₂, and H₂ to then produce ethanol, acetic acid and other byproducts such as lactate, 2,3-butanediol, butanol, butyrate, and acetone¹⁸.

The WLP shown in detail in **Figure 1** can be seen to consist of two main pathways, known individually as the methyl and carbonyl branch, both leading to the formation of the primary intermediary chemical in the pathway – acetyl-CoA¹⁷. Acetyl-CoA, in this case, serves as a precursor molecule for the formation of an array of cell macromolecules, while also acting as an adenosine triphosphate (ATP) reserve for the cell¹⁹. One of the key distinction of syngas fermenting microbes is their ability to omit the requirement of a sugar-based substrate in its

entirety. In other words, WLP can operate independent of the glycolytic pathway, either as a primary or auxiliary metabolic pathway. In the presence of sugary substrates, WLP serves as an auxiliary pathway to further increase the carbon utilization efficiency of sugar substrates by converting CO_2 released by the glycolytic pathway to additional Acetyl-CoA. If only CO is present to the microbes as the substrate, 2 molecules of CO enter the pathway simultaneously, one entering the carbonyl branch, while the other enters the methyl branch and will be oxidized to CO_2 before being converted into a methyl group in subsequent reactions. If only CO_2 is present to the microbes as substrate, 2 molecules of CO_2 will also enter the pathway simultaneously, one molecule will be stepwise reduced to a methyl group via the methyl branch, skipping the aforementioned step where CO undergoes oxidation to CO_2 , while the other enters in the carbonyl branch, with CO_2 being reduced to CO.

Overall, in the WLP, CO or CO_2 is reduced to a methyl group through a series of reductive reactions in the presence of several hydro folate-dependent enzymes and at the expense of an ATP through the methyl branch, while carbonyl group is being prepared through the carbonyl branch with the aid of carbon monoxide dehydrogenase complex (CODH)^{17,18}. The resulting methyl and carbonyl groups will then be combined by the enzyme acetyl-CoA synthase (ACS), together with Coenzyme A to produce acetyl-CoA¹⁷. Acetyl-CoA can then be further reduced to a variety of metabolites in the subsequent stages in the pathway¹⁹.

Additionally, as reduced ferredoxin (Fd^{2-}) is an integral aspect of both the methyl and carbonyl branch, the microbes would, therefore, require electron sources for the reduction¹⁷. In the absence of H_2 gas, CO will also act as an electron source on top of its role as a substrate through its oxidation to CO_2 which directly simultaneously form Fd^{2-} . In the presence of H_2 , however, the microbes will then use H_2 as an electron source with the aid of an electron bifurcating hydrogenase in converting 2 H_2 molecules to obtain Fd^{2-} and a reduced nicotinamide adenine dinucleotide (NADH)¹⁷.

In relation to the reasoning discussed in previous sections, focusing specifically on ethanol and acetate production, which also often are the primary metabolites of these syngas fermenting microbes, to produce acetate, acetyl-CoA will then be converted by the enzymes phosphotransacetylase (PTA) and acetate kinase (ACK) to form acetate, resulting in the release of one ATP molecule, therefore balancing the ATP consumed in the methyl branch¹⁷. As for the production of ethanol, the previously formed reduced NADH from the reduction of ferredoxin which must be consumed in one of the subsequent reactions would then be

consumed in the production of ethanol. Similarly, the same NADH can also be consumed through the formation of other products, such as butanol, 2,3-butanediol, or back through the reductive pathway along the methyl branch¹⁷.

Design Parameters

Objectives

Based on the previous elaboration, this thesis, therefore, aims to report an attempt in designing a biocatalytic process for steel mill waste gas recovery, utilizing fermentative methods in producing ethanol of at least 99% purity as a primary product.

Steel-mill off-gas stream specification

For the purpose of the design elaborated in the subsequent chapters, a value of 6 million metric tons of annual steel production was assumed. According to the previously mentioned correlation between waste gas emission and steel production of 1.8 metric tons of waste gas per ton of steel production⁶, the design reported in this thesis aims to process the entire waste gas stream, totaling at 10.8 million metric tons of waste gas emission annually, thus averaging at approximately 342 kg/s of mass flow rate of steel mill off-gases flowing in at a temperature of 25°C and atmospheric pressure. In terms of composition, the waste gas stream in this design is taken to consist of 99 wt% of primary components, such as CO (30 wt%), CO₂(14 wt%), H₂(15 wt%), N₂(35 wt%), and CH₄(5 wt%), and 1 wt% of impurities, such as NO, SO₂, H₂O, NH₃, H₂S, and tar, each present in 1:1 wt% ratio to each other. Additionally, carbon solid particles were also included as a part of the impurities in the waste gas stream, present also at 1:1 wt% ratio to the other gaseous impurities in the waste gas stream. The complete waste gas specification and composition, both in terms of mass fraction and the corresponding mole flow can be found to be summarized in **Table 2**.

Temperature: 25°C

Pressure: 1 bar

Component	Mass fraction	Flow (mol/s)
CO	3.0E-01	3665.4
CO ₂	1.4E-01	1088.7
H ₂	1.5E-01	25465.2
N ₂	3.5E-01	4275.8
CH ₄	5.0E-02	1066.6
NO	1.7E-03	19.0
SO ₂	1.7E-03	8.9
H ₂ O	1.7E-03	31.7
NH ₃	1.7E-03	33.5
H ₂ S	1.7E-03	16.7
Tar	1.7E-03	4.4E-06
Carbon (s)	1.7E-03	4.4E-06

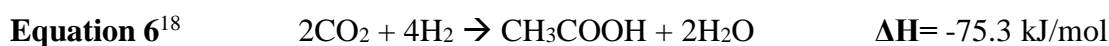
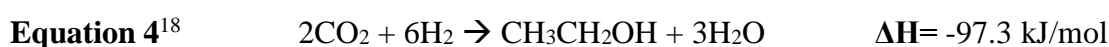
Table 2. Steel mill waste gas specification and composition

Biocatalyst specifications

For the purpose of the design which will be described in the subsequent chapters, the process uses *Clostridium ljungdahlii*, a rod shape, gram-positive anaerobic bacteria, as the microbe of choice in the biocatalytic process. One of the main consideration in choosing the said biocatalyst is that *C. ljungdahlii*, discovered in 1987, has been known to be one of the very first microbes found to exhibit the previously explained WLP, which is required in achieving the objective of the design reported in this thesis. *C. ljungdahlii* is therefore known as the paradigm in similar biocatalytic syngas conversion process, thus have been extensively documented and studied throughout the years. Furthermore, *C. ljungdahlii* has also been known to form primary metabolites, being mostly acetate and ethanol, from CO, CO₂, and H₂.

In this design, however, the specific strand of the aforementioned microbes will intentionally be left unspecified. This choice is made mainly due to the large variety of strands one can choose from, particularly for the said microbe. The design, therefore, assumes that the specific strand of the *C. ljungdahlii* used in the design have undergone genetic tuning procedure, such that it works optimally within the process conditions of this study. In an attempt to further streamline the process design, more specifically the work-up processes, the aforementioned

genetic optimization also assumed to include the suppression of the pathways leading to the formation of metabolites other than ethanol and acetate. This, therefore, implies that the process reported in this thesis is tailored for a biocatalytic process producing exclusively ethanol and acetate. As a consequence of this assumption, the overall biochemical reactions which take place throughout the process, via the reductive acetyl-CoA pathway, can be summarized by stoichiometric reaction equations shown in **Equation 3 - Equation 6**, along with their corresponding standard reaction enthalpy (298K, 1 bar), with the reactant of reference being either CO or CO₂.



Additionally, due to the scarcity of information regarding the exact kinetic relation for the specific microbe at specific design conditions, the reported design would assume an unknown reaction kinetics to be significantly faster relative to the mass transfer rate of the reactants from the gas to the liquid phase. This, therefore, implies that the productivity of the process reported in this thesis would only be mass transfer limited within the design conditions of the reported process. Furthermore, due to limited availability of comparable data points on similar process productivity, the design also assumes a productivity value that is independent of the product and reactant concentration and their equilibrium relationship.

Chapter II - PROCESS DESIGN

Reactor Design

Process design in this system revolves around the method chosen to ferment syngas to ethanol. A different approach comes with different system stipulations, making reactor choice and design the most influential aspects of the process. Reactor design will therefore be treated first, after which the syngas requirements and product streams will become clear, allowing the syngas cleanup and product purification designs to follow.

Reactor criteria and design

Microbial bio-reactors all face challenges typically not encountered in conventional chemical process design. Microbes in such processes are analogues to catalysts, except very fragile catalysts, that are living, growing, dying, and simultaneously very susceptible to changes in pressure and temperature. As touched upon in the introduction, microbial catalysts do present significant advantages too, such as their ability to achieve fairly complex chemistry at low temperatures and pressure, and their ability to grow, something every chemical engineer wishes their expensive catalysts could do with simple nutrition. Microbial bio-reactors must take into account the sensitivities of microbes to pressure and temperature change, and their very finite life cycles, considerations that will affect the chemical process design.

Discussed in literature are two methods for producing ethanol via syngas fermentation, batch and continuous processes. Both choices account for the life cycle of microbes. The batch reactor process starts and ends with the life-cycle of the microbes, and a continuous process introduces new cell culture, and purges old cell medium to maintain a healthy cell body. Due to the continuous syngas stream utilized in this plant, a continuous process system was sought.

Clostridium ljungdahlii

To cater to *C.ljungdahlii*, one needs to understand the conditions preferred by the microbe and its reaction kinetics. Primarily, *C.ljungdahlii* is mesophilic, and primarily produces ethanol and acetate^{20 21}. *C.ljungdahlii* growth and reaction kinetics are strongly affected by pH, with a pH of near 6 promoting growth and acidogenesis, and a lower pH of 4.5 promoting solventogenesis, but discouraging growth^{1 22}. Acidogenesis and solventogenesis describe the kinetic pathway promoted at each pH, where acidogenesis describes acetic acid production, and solventogenesis ethanol. Under both acidogenesis and solventogenesis, acetic acid and ethanol are both produced, but one is produced in excess. For *C.ljungdahlii*, Acetic acid is

produced at a ratio of 13:1 in a growth promoting pH near 6, and ethanol is promoted at a ratio of 5.5:1 in the solventogenesis promoting pH 4.5 region.²² Use of *C.ljungdahlii* means both conditions will need to be met in order to both grow the microbes, and promote ethanol production, the target product.

Previous applications

C.ljungdahlii among other syngas fermenting microbes are not novel, and publications on the subject date back to the early 1990s²³. Wide spread application of such processes are to date limited, and no commercial applications exist on a comparable scale to this design. Focus was therefore applied to many well documented lab-scale reactors, which unlike commercial examples, published extensive data on the lab-reactor workings and parameters. With consideration of the aforementioned stipulations imposed by *C.ljungdahlii*, our process requirements, and desired process product, a lab-scale reactor designed at Cornell University in 2013 was chosen as the primary basis for our process design.

Reactor Choice

In an August 2013 publication by the Department of Biological and Environmental Engineering at Cornell University, a two-stage bio-reactor for the conversion of syngas to ethanol was presented.

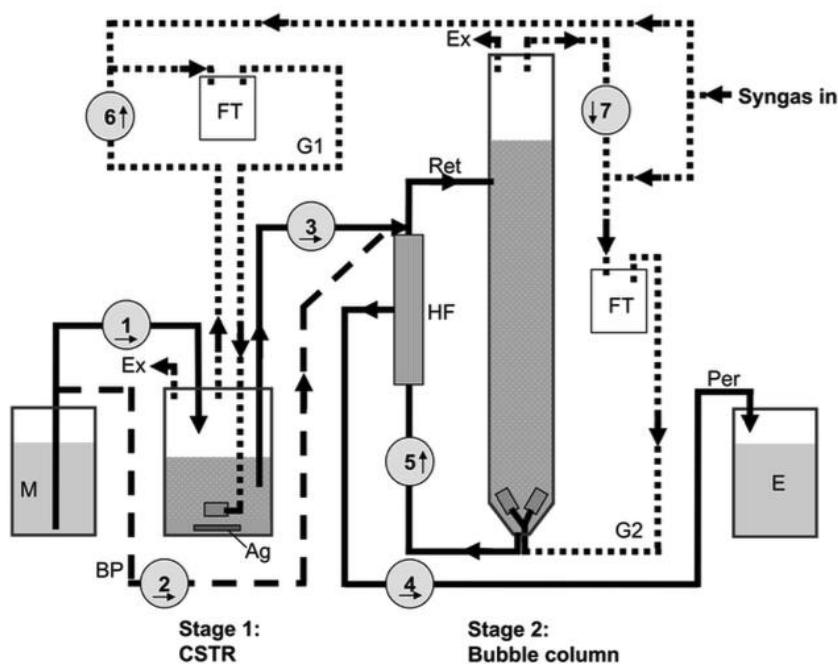


Figure 2: Setup of two-stage continuous fermentation with cell and gas recycle. Solid lines: flow of liquid media; dotted lines: flow of substrate and exhaust gases. Abbreviations: 1–7 pumps; Ag, agitation; BP, bypass; E, effluent reservoir; Ex, exhaust; FT, foam trap; G1, G2, gas recycle loops; HF, hollow fiber module for cell recycle; M, media reservoir; Per, permeate; Ret, retentate²².

The reactor shown in **Figure 2** overcomes all the aforementioned challenges in a few key steps. Primarily, it utilizes two reactors, each held at a different pH, to promote growth, then production. The system not only fosters acidogenesis, then solventogenesis, but also filters cells, purging and recycling a fraction of the filtered cells to maintain homogeneity within the system. Their design consists of a 1L CSTR for growth, and a 4L bubble column for production. Cornell's system operated both stages at 1bar, and used a syngas inlet of 60vol.% CO, 35vol.% H₂, 5vol.% CO₂. The principle of the reactor is that cell medium, which includes cell inoculation media and nutrients for growth is introduced from M, the Medium reservoir into Stage 1, the growth stage. The growth stage pH is controlled by action of acid or base pumps, and cells grow whilst producing acetate and some ethanol. Syngas is bubbled through the bottom of the CSTR, and dissolves into the liquid media. Once dissolved, the microbes can access the gas for ethanol or acetate production. Stage 1 medium is pumped into stage 2, where the pH is again controlled by acid or base pumps, and ethanol production is promoted. Finally, a hollow membrane filters cells from the stage 2 liquid medium, and cell free product is pumped to a reservoir²².

Detailed information regarding their gas inlet concentration, absorption, and production of acetate and ethanol in each stage was provided, alongside detailed growth rate information, nutrient supply, and microbe productivity.

Compounds	Rates [mmol/(L·min)]		
	Stage 1	Stage 2	Total
CO in	0.607	0.808	0.768
CO out	0.33	0.11	0.154
CO consumption	0.277	0.698	0.614
H ₂ in	0.354	0.471	0.448
H ₂ out	0.182	0.085	0.105
H ₂ consumption	0.172	0.386	0.343
CO ₂ in	0.051	0.067	0.064
CO ₂ out	0.085	0.371	0.314
CO ₂ production	0.034	0.303	0.25
Ethanol production	0.007	0.136	0.11
Acetic acid production	0.094	0.025	0.039

Table 3: Syngas inflow, outflow, and consumption, and Ethanol and Acetic acid production, per stage of lab-scale plant.

To compare the applicability of Cornell's lab scale plant to the target syngas feed, and whether the lab scale plant lends itself well to upscale, some initial estimates were made. Primarily, one may estimate the scale of a syngas fermentation plant needed to process the utilized syngas feed in this process. Using **Table 3**, it was found that the mol flow per unit volume used on this scale was $1.28 \frac{\text{mmol}}{\text{L} \cdot \text{min}}$, or $0.0213 \frac{\text{mol}}{\text{m}^3 \text{s}}$. Mentioned in the introduction is the need to convert a $342.23 \frac{\text{kg}}{\text{s}}$ syngas flow. With information provided on the contents of said gas flow, the molar flow rates of various components was derived.

Component	Fraction	$\frac{kg}{s}$	$\frac{kg}{mol}$	$\frac{mol}{s}$
H2	0.15	51.3	2.02 E-3	25413
N2	0.35	119.8	2.80 E-2	4276
CO	0.30	102.7	2.80 E-2	3666
CO2	0.14	47.9	4.40 E-2	1089
CH4	0.05	17.1	1.60 E-2	1067
Impurities	0.01	3.4	Total	35510

Table 4: Derivation of molar inflow of syngas excluding impurities.

With an established molar inflow of $35510 \frac{mol}{s}$, and a known mol flow per unit volume of $0.0213 \frac{mol}{m^3 s}$ for Cornell's reactor setup, an estimated net volume of 1.7 million m^3 was reached. Note, since the gas composition used in this system is poorer in terms of CO and CO₂ than Cornell's feed, this value would in reality be bigger. Nonetheless, this "upscale" still provides useful information. Using height to diameter ratios appropriate for bubble columns, the height of our new setup would rival that of the Eiffel tower. With that, the main challenge to working with microbes is insinuated, their relatively low productivity in ambient conditions. Cornell's lab scale reactor reached a productivity of $0.374 \frac{g}{L h}$ of ethanol. This is fairly high when compared to other cited productivities, but higher productivities in different systems have been achieved. The problem encountered here is however not intrinsic to Cornell's system, so searching for an alternative process would yield similarly large equipment.

In order to achieve a workable design, it became clear that the productivity per unit volume of the system would need to be increased. In doing so, one needs to be mindful of the scientific viability of the upscale, and therefore every assumption and upscaling factor should be supported by experimental evidence or scientific theory to ensure an upscale with a footing in the scientific realm.

Process Upscale and Optimization

As shown in *Reactor Choice*, a lot of ground must be covered in order to bring the productivity and viability of this system into realization. To not limit the design process, and since the aim of this evaluation is to determine if the process in mind is viable, no economic restrictions were

set in the design phase, and rather an economic evaluation after the fact will determine whether the derived system would be economically effective.

Primarily, focus was applied on the limiting factor in product formation by establishing whether the process was mass solvent transfer limited, microbe transfer limited, or kinetically limited. If the microbes were kinetically limited, or mass transfer limited through their cell membranes (microbe transfer limited), the viability of this system would be hampered, as less can be done to increase the production speed of the microbes, or mass transfer through their cell membranes than can be done to increase the mass transfer rate of the syngas into the liquid medium.

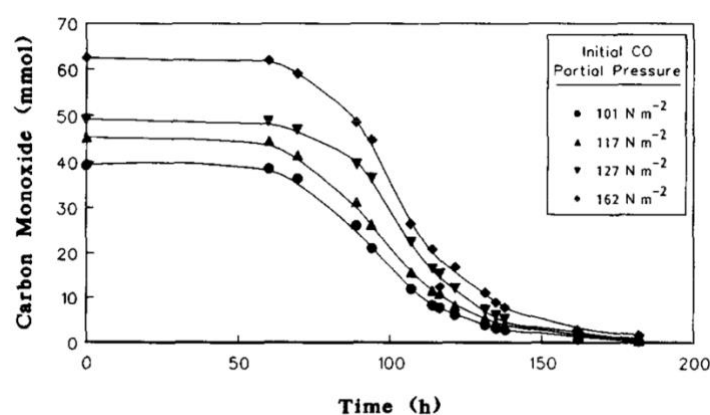


Figure 3: CO profile for the fermentation of CO by *C.ljungdahlii*

A study by the University of Arkansas followed the change in partial pressure of CO over time starting from different initial partial pressures, and as shown in **Figure 3**, and found the rate of consumption of CO was affected by the initial partial pressure of CO in the system. This is illustrated by the increased slope of the lines representing the partial pressure as a function of time. This data insinuates the microbes were not kinetically limited or mass transfer limited through their membranes, but rather mass transfer limited under these test pressures. In a separate study at the University of La Coruña, researchers varied the total pressure applied to a culture of *C.ljungdahlii* between 0.8 and 1.6 bar in a batch reactor, and found that doubling the pressure resulted in a 3.6 fold increase in ethanol production²⁴.

Due to these findings, the assumption that this process is only mass transfer limited to solvent is adopted. This means that increasing the mass transfer rate of syngas into the liquid will be the aim to increase productivity.

To summarize, there were three possible limiting factors considered for microbe productivity, namely mass transfer to the solvent, mass transfer to the microbe through its cell wall, and then the rate of production within the microbe. Next, consultation of data from two different sources both suggested that an increase in pressure resulted in an increase in production, or increased consumption of CO. This means that under the test conditions of these experiments, the limitation of the microbe's productivity was not the cell wall mass transfer rate, nor the production speed of the microbes itself.

Because mass transfer to the solvent can be hugely increased by increasing system pressure, eventually, a mass transfer limitation would be found in the cell wall mass transfer rate of the microbes, or the production rate of the microbes. However, for the purpose of upscale, because the system pressure will not be increased to unreasonably high pressures, and because no consulted literature discussed kinetic limitations or mass transfer limitation in the cell wall of *C. ljungdahlii*, the possibility of cell wall mass transfer limitations or production rate limitations will not be considered for this upscale.

This decision translates into a more practical assumption, that if the microbes can consume dissolved gasses faster than they can be dissolved, that the steady state bulk concentration of consumed gasses in the liquid is 0.

The molar flux into a liquid is given by J_A . The equation for J_A is shown below.

$$J_A = \left(\frac{c_{AG} - \frac{c_{AL}}{m}}{\frac{1}{k_g} + \frac{1}{k_L * m}} \right) \quad (\text{Equation 7}), \quad Abs = J_A * A \quad (\text{Equation 8})$$

Equation 7: Mol flux

Equation 8: Absorption

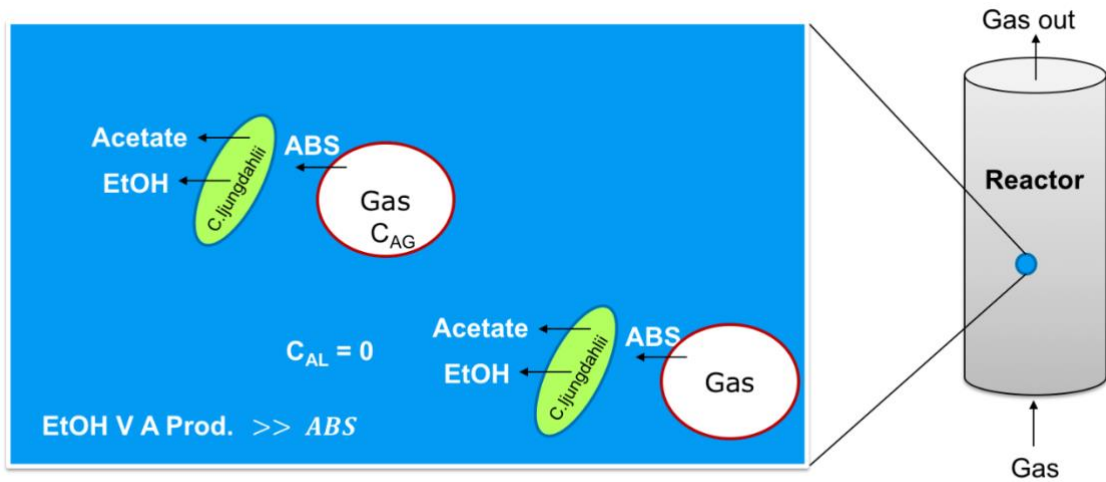


Figure 4: Visual illustration of syngas absorption and product production by *C.ljungdahlii*

The assumptions that the reaction is not kinetically nor cell wall limited implies the microbes will convert all gasses diffused into the liquid at a greater rate than they can be diffused, which means the bulk concentration of gas in the liquid is assumed to be zero.

This allows one to simplify **Equation 7**.

$$J_A = C_{AG} \left(\frac{1}{k_g} + \frac{1}{k_L * m} \right)^{-1} \quad (\text{Equation 9})$$

Equation 9: Simplified mol flux equation assuming CAL bulk is zero.

Assuming the mass transfer coefficients of the gas and liquid are constant (k_g and k_L), and the partition coefficient m is also constant, J_A becomes proportional to C_{AG} .

$$c_{AG} = \frac{P}{RT} \quad (\text{Equation 10}), \quad c_{AG} = f(P), \quad c_{AG} \sim P$$

Equation 10: C_{AG} (concentration of A in gas) as per Ideal Gas Law

With J_A proportional to C_{AG} , and C_{AG} proportional to P (pressure), molar absorption (**Equation 8**) is proportional to P assuming constant contact area.

$$Abs = J_A * A = \left(\left(\frac{P}{RT} \right) \left(\frac{1}{k_g} + \frac{1}{k_L * m} \right)^{-1} \right) * A \quad (\text{Equation 11})$$

Equation 11: Modified absorption equation from Equation 9 and Equation 10.

The problem with assuming constant contact area is that the area of a given gas is proportional to the size of the rising bubbles in the reactors or amount of bubbles rising in the reactor. As the system pressure increases, the gas is compressed, and a molar flow of gas at high pressure would have a smaller volume compared to said mol flow in a low-pressure system.

$$\phi_V = \frac{m^3}{s} = \frac{\phi_{mol} MW}{\rho} \quad (\text{Equation 12}), \quad DA: \frac{mol}{s} * \frac{kg}{mol} * \frac{m^3}{kg}$$

$$\rho = \frac{kg}{m^3} = \frac{n MW}{V} = \frac{P MW}{RT} \quad (\text{Equation 13}), \quad \text{Ideal Gas law}$$

$$(\text{Equation 12}) + (\text{Equation 13}) = \phi_V = \frac{\phi_{mol} MW RT}{P MW} = \frac{\phi_{mol} RT}{P} \quad (\text{Equation 14})$$

Equation 12: Volumetric flow in terms of mol flow and density

Equation 13: Density (ρ) derivation as per ideal gas law

Equation 14: Equation for volumetric flow in terms or mol flow and pressure and temperature. Note: Mw = Molecular weight.

As shown in **Equation 14**, volumetric flow is a function of mol flow, pressure, and temperature. Since the system temperature will be kept constant, $\phi_V \sim \phi_{mol}$, $\phi_V \sim \frac{1}{P}$, meaning ϕ_V can be kept constant assuming molar flow is scaled with pressure.

This can be shown to be the case when looking specifically at the formula that determines the volume of bubbles from a sparger.

$$V_B = \frac{2\pi R\sigma}{g\Delta\rho} \text{ (Equation 15)}$$

V_B = Volume of bubble (mL V cm³)

R = orifice radius (cm)

σ = surface tension (dynes/cm)

g = gravitational constant (cm/s²)

$\Delta\rho$ = density of liquid – density of gas within bubble

Equation 15: Volume of bubble in column from sparger formula²⁵

As shown in **Equation 15**, the volume of a bubble is proportional to the size of the orifice of the sparger, and inversely proportional to the pressure difference between the bubble and exterior liquid. The other variables are considered constant. In order to maintain a gas flow, the pressure within the bubble will need to be increased to an extent that allows the gas to flow through the sparger and create a bubble. Because of this, a change in system pressure, or liquid pressure in the reactor, will need to be reflected in a change in pressure of the exiting bubbles from the sparger. This translates to constant bubble size when using a sparger, since the orifice radius R is constant. What will change upon pressure increase is then the number of bubbles that exits the sparger. This is because to increase the pressure within the bubbles exiting the sparger, the inlet gas must be compressed, and this compression reduces the volume of incoming gas. Therefore, the notion that a constant volume flow when increasing pressure must be accompanied by a proportional mol flow increase is supported through **Equation 15**.

If the system is scaled as such, then the volume of all bubbles, and the volume of individual bubbles should remain constant, which allows for a constant contact area in **Equation 11**. Following these guidelines, molar flux, and therefore absorption into the liquid is proportional to pressure so long as molar inflow per reactor is scaled with pressure.

Syngas Optimization

With a viable upscale method in place, attention can be drawn to the syngas composition. In order to determine absorption data, empirical data will not be sourced to derive J_A , and estimate the contact area in the lab-scale plant. Instead, using the absorption rate and efficiencies divulged in the literature summary of Cornell's plant, the absorption rates of the gasses in this system's syngas will be estimated, after application of correction factors to account for the different concentrations and partial pressures between the two syngas inlets.

Component	Vol % (lit)	Vol % (design)
H ₂	35.00	71.57
N ₂	-	12.04
CO	60.00	10.32
CO ₂	5.00	3.07
CH ₄	-	3.00

Table 5: Comparison of Cornell plant syngas feed vs design feed. (Not including impurities)

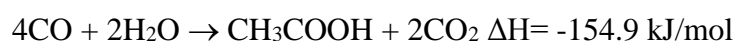
To understand if the syngas feed can be optimized, one must look at the microbial requirements for ethanol and acetic acid production. As per the introduction, the reactions considered in the pathway are as follows.



Equation 16



Equation 17



Equation 18



Equation 19

Equation 16 - Equation 19: Considered reactions for the fermentation of syngas to ethanol and acetate by *C.ljungdahlii*.

As per **Equation 16 - Equation 19**, the carbon source for ethanol and acetate production is from CO and CO₂. In the literature feed, both compounds make up 65vol.% of the inlet, whilst in the current design, only 13.4vol.% of the inlet consists of the carbon source. Additionally, the current design has a 71.5vol.% H₂ feed, whilst the Cornell's plant had a 35vol.% H₂ feed. The volume fraction or molar fraction (which are equivalent in the gas phase) are directly proportional to the concentration or abundance of a gas in a given atmosphere, where a larger fraction X_A is achieved at a higher partial pressure of a given gas.

$$X_A = \frac{P_A}{P_T} \text{ (Equation 20)}$$

Equation 20: Fraction of gas A. P_A = Partial pressure of A. P_T = System's total pressure.

As per **Equation 20**, reducing the amount of unneeded gas, which in turn boosts the partial pressures of relevant gasses, is favorable, as that would increase the concentration of relevant gasses, and in turn increase the mol flux of said gasses. An ideal syngas feed was then derived assuming 100% conversion of components, and using ideal stoichiometry (**Equation 16 - Equation 19**) with consideration of stage production ratios (*Clostridium ljungdahlii*, 17). Remco, the gas cleaning engineer, was also consulted in this process, and **Table 6** resulted.

	Current	Current	Target	Target
Compound	mol/s	Vol % or mol%	mol/s	Vol % or mol%
H2	25413.22	71.57	11427.51	65.92
N2	4275.91	12.04	42.76	0.25
CO	3665.46	10.32	5846.01	33.72
CO2	1088.68	3.07	2.00	0.01
CH4	1066.81	3.00	17.00	0.10

Table 6: Determined syngas cleaning target values per compound in mol/s

Remco, the gas cleaning engineer, indicated additional CO would be formed, alongside a reduction of CO₂ and CH₄ in his initial clean up, hence the deviation in values of CO, CO₂ and CH₄ from the original feed. A notable feature of **Table 6** is that a lot less hydrogen is needed than is already present in the feed. Knowledge of membrane filtration for N₂ removal resulted in a 99% removal estimate of N₂, and with that a target syngas feed was created. The final calculations to determine the exact stoichiometric need of H₂ was achieved via excel. This was more complicated as each reactor produced different products due to the different pH and

product ratios in each reactor. This is relevant because the production of acetate involves 4 hydrogens, in contrast to the production of ethanol that requires 6. Therefore, separate ideal feed inlets were designed per stage, which sum to the values depicted in **Table 6**. Not explicitly noted here is the ask that Remco removes ash, tar, and other impurities that may contaminate the microbe population. Because the molar flow of impurities depends on the molecular weight chosen for the tar, or carbon-ash, and additional impurities, the flows have not been explicitly stated in **Table 6**, but as per **Table 4**, $3.42 \frac{kg}{s}$ of impurities are expected.

With the specifications of the target syngas feed determined, an upscale for the plant may be attempted to determine the product output for future product purification. Since at the stage of the upscale, a true syngas feed had not been determined by the syngas cleanup engineer Remco, some guess work was involved to form a usable syngas stream that could be used for the scale up. This was necessary as many aspects of the design are influenced by the syngas feed and changing the inlet at every change in the syngas engineers design would be unfeasible. At the time the upscale parted ways from Remco's influence, an inlet syngas composition was determined as per **Table 7**.

Element	mol/s	Vol %
H2	11427.51	52.98
N2	4275.91	19.82
CO	5846.01	27.10
CO2	2.00	0.01
CH4	17.00	0.08

Table 7: Used mol flow for upscale.

To determine upscale parameters, the inlet syngas was split at a ratio of $1:1.33 \frac{mmol}{L s}$, or 1:5.18 mol ratio between stage 1 and 2 when accounting for the difference in stage volumes as per Cornell's system. This allowed one to derive the syngas inlet per stage.

Compound	Flow (mol/s)		Compound Vol%	
	Stage 1	Stage 2	Stage 1	Stage 2
H2	1012.82	10414.69	38.19	55.06
N2	691.09	3584.81	26.06	18.95
CO	944.86	4901.15	35.63	25.91
CO2	0.32	1.68	0.01	0.01
CH4	2.75	14.25	0.10	0.08

Table 8: Mol flow and volume composition of syngas derived for stage 1 and stage 2 or reactor setup.

With a known absorption efficiency for each compound derived from Cornell's pilot plant, these absorptions efficiencies can be applied to the compounds in this new feed to determine their absorptions efficiencies. The principle behind this is that if CO made up 10vol.% of one's inlet was consumed at a 20% efficiency, if one changed CO's volumetric inflow to 20vol.%, CO would be twice as abundant, and consumed twice as much, meaning it would also diffuse twice as readily. This translates to a doubling in the consumption efficiency of CO as compared to the initial system. Since the systems diffusion efficiencies are provided in Cornell's upscale, one can determine efficiency correction factors (X) by comparing the abundance of gasses in the new feed to Cornell's original feed. In doing so, **Table 9** is derived.

Element	Literature Gas inlet volume	Reactor Gas inlet Volume		Correction Factor (X)	
	Stage 1&2	Stage 1	Stage 2	Stage 1	Stage 2
CO	60	0.36	0.26	1.68	2.32
H2	35	0.38	0.55	0.92	0.64
CO2	5	1.22E-04	8.86E-05	410.18	564.08

Table 9: Correction factor to be applied to diffusion efficiencies per relevant compound of stage 1 and 2.

Note, the correction factor (X) is applied to the absorption efficiency of each gas in the following way.

$$\text{New Abs efficiency} = \text{Lit. Abs Efficiency} * \left(\frac{1}{X}\right)$$

Equation 14: New Abs efficiency formula.

Element	Lit. 1-pass ABS Efficiency		New 1-pass ABS efficiency	
	Stage 1	Stage 2	Stage 1	Stage 2
CO	0.46	0.86	0.27	0.37
H ₂	0.49	0.82	0.53	0.76
CO ₂	N/A	N/A	1.00	1.00

Table 10: Literature vs corrected absorption efficiencies.

Note, CO₂'s absorption efficiency was not provided or deducible from literature. This is because in literature more CO₂ is produced than consumed in the reactors. This is not considered the case in this upscale as the value of incoming CO₂ is very low, and therefore produced CO₂ is presumed to dissolve and contribute of product production. Additionally, with consultation of Henry's law, CO₂ is found to be 8.5 times more soluble in water than CO, and is therefore assumed to fully dissolve. Therefore, CO₂ diffusion efficiency is assumed 1²⁷.

Table 10 demonstrates that under the conditions of the Cornell design, assuming no changes other than the syngas feed composition, each gas would diffuse into the liquid medium at the efficiencies stated. Now suppose the pressure doubled. The concentration of each gas would double, meaning twice as much gas could diffuse into the liquid medium of the reactor. To increase the efficiency of the stages, one may increase the gas residence time too. Doubling reactor volumes vertically (to ensure the residence time of the gas bubble is doubled) means the amount of gas that can be diffused also doubles, as the gas has twice the time and opportunity to diffuse per pass. The benefit of increasing pressure over increasing gas residence time is that higher pressure means more moles of gas can be pushed through a given reactor. This reduces the overall reactor size, which makes doubling the gas residence time more feasible as the reactor is smaller. Based on **Table 10**, the lowest efficiency is that of CO in stage 1, where in a single pass, only 27% of the CO is converted. In order for all gasses to achieve a 100% theoretical efficiency based on this upscale, an increase of about 4x diffusion, or productivity must be attained. To exist safely within this threshold, the pressure in the upscaled plant is increased to 10bar, and the gas residence time is doubled. This is beneficial, as increasing the pressure more than necessary allows for a smaller net plant size and as a greater mol flow is packed into each reactor.

With the net syngas conversion per reactor known, and the diffusion, which in this case is equal to consumption, known, the fractional conversion of each stage can be derived, as it now equals the ratio of acetate to ethanol produced in each stage according to literature.

Reactions	Prod. Of (EtOH or AA) (based on 1-pass efficiency) (mol/s)	
	Stage 1	Stage 2
$6 \text{ CO} + 3 \text{ H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 4 \text{ CO}_2$	13.23	777.96
$2 \text{ CO}_2 + 6 \text{ H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 3 \text{ H}_2\text{O}$	20.42	1538.20
$4 \text{ CO} + 2 \text{ H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2 \text{ CO}_2$	216.37	58.35
$2 \text{ CO}_2 + 4 \text{ H}_2 \rightarrow \text{CH}_3\text{COOH} + 2 \text{ H}_2\text{O}$	222.57	76.91

Table 11: Stage 1 and stage 2 production of ethanol and acetate per reaction

Table 11 displays based on 100% gas conversion and a 13:1 (Acetic acid: Ethanol) product ratio in stage 1, and 20:1 (Ethanol: Acetic acid) conversion in stage 2, the moles of ethanol or acetic acid made per reaction per stage. As mentioned under *Clostridium ljungdahlii*, different pH conditions influence the product ratio of Ethanol:Acetic acid made in each stage. Though the Cornell plant only achieved a 5.4:1 Ethanol:Acetic acid mol ratio in stage 2, it is well documented in literature that under the correct conditions, the optimum ratio attainable is a 20:1 Ethanol:Acetic acid mol, and since ethanol is the target product, said ratio is used in this design.

Syngas in (Original) (mmol/L*s)		New pressure (bar)	Syngas in (New) mmol/L*S		Production increase factor
Stage 1	stage 2		Stage 1	stage 2	
0.01687	0.0224	10	0.1687	0.2243	20
		Gas res time scale factor			Volume increase factor
		2			2

Table 12: Pressure increase, gas res time increase, and resulting new syngas inflow allowed under new process conditions.

As per **Table 11** and **Table 12**, the volume of the total plant can be deduced, and to limit the size of each reactor, a final design of 5 parallel plants was chosen. This would split the total needed volume to 900m^3 (830m^3 liquid vol) for the stage 1 CSTR of each plant, and 3500m^3 (3225m^3 liquid vol) for the stage 2 bubble column. To finalize an upscale, the dilution rate must be calculated to determine both the liquid inflow into the reactors, which affects the pumping specs of the reactor, and the final steady state concentration of ethanol in the final product. It is important to control the steady state concentration of EtOH as a too high alcohol content in the reactors would affect reaction kinetic. A threshold of roughly 10% was decided as the target steady state concentration.

As per the excel calculator that approximates this system, a volumetric inflow of $977 \frac{m^3}{h}$ was derived. This gives a liquid residence time of 1h and 3.3h in stage 1 and 2 respectively. This is very fast compared to the residence time of 25h and 100h in the Cornell's plant, but this is believed not to influence the production of the system, but rather the degree of cell recycling. This is because the only effect of a shorter residence time is that in a cells life time, it will need to pass through the growth reactor, then production reactor more times than it would had the residence time been greater. This increased cycling is not expected to have adverse effects on the microbes, as cells would cycle through both conditions naturally, and no literature encountered discussed adverse effects of such cycling. Additionally, single stage continuous processes exist where the pH in the reactor is altered from high to low pH to temporality encourage growth, then ethanol production, insinuating the microbes are capable of withstanding pH cycling. The theoretical upscale via excel is completed with a final prediction of the final steady state concentrations for each reactor output.

	Water	Ethanol	Acetate
Mol fraction	9.64E-01	3.45E-02	1.72E-03
Vol %	89.19	10.30	0.51

Table 13: Excel predicted product output in mol and vol. %

Total Outlet (mol/s)		
Water	Ethanol	Acetate
77859	2785	139

Table 14: Final production values of water, ethanol, and acetate in mol/s

With the design parameters of the production stage complete, and an approximation of both syngas requirements and product output parameters, the syngas cleanup engineer Remco can design a syngas cleanup stage, further design elements and calculations can be made on the reactor section, and the purification specialist Patrick may begin work on designing the product purification plant. Additionally, Aspen can now be used to approximate the results deduced here, and build on the current model of the process to develop a more comprehensive understanding of the process.

Auxiliary Calculations

Though an approximation has been made to reflect the reactors production and needs, calculations must be made to approximate the steady state needs of auxiliary flows into the reactor. Cell cultures once acquired can be maintained at healthy populations by growing more cell culture with the use of nutrients, and the only required flows left to be deduced is the steady state nutrient flow into the reactor to sustain the microbes. According to literature, a nutrient stock is added to the growth reactor at a 1:16 volume ratio as compared to the water inlet²². The nutrient stock consists of a pH buffer, a mineral stock, vitamin stock, trace metal stock, and an antifoam agent, antifoam 204²⁸. During steady state operation, the nutrient stock contains the chemicals listed in **Table 15** at the indicated concentrations, and the nutrient medium flow accounts for $57.5 \frac{m^3}{h}$ of the $977 \frac{m^3}{h}$ water inflow.

	Chemical	L/m3	Annual Consumption (L)
	Antifoam 204	2.5E-01	125860.59
	Chemical	kg/m3	Annual Consumption (kg)
General	Yeast Extract	7.8E-02	39331.43
	(MES)*	7.8E-01	393314.34
Mineral Stock ²⁹	sodium chloride	9.4E-01	471977.21
	ammonium chloride	9.4E-02	47197.72
	potassium chloride	9.4E-02	47197.72
	potassium monophosphate	1.9E-01	94395.44
	magnesium sulfate	3.8E-02	18879.09
	calcium chloride	6.3E-05	31.47
Vitamin Stock ¹⁵	pyridoxine	6.3E-05	31.47
	thiamine acid,	3.1E-05	15.73
	riboflavin	3.1E-05	15.73
	calcium pantothenate	3.1E-05	15.73
	thioctic acid	3.1E-05	15.73
	paraamino benzoic	3.1E-05	15.73
	nicotinic acid	3.1E-05	15.73
	B12	3.1E-05	15.73
	d-biotin,	1.3E-05	6.29
	folic acid	1.3E-05	6.29
Trace Metal Stock ¹⁵	2-mercaptoethanesulfonic acid	1.3E-05	6.29
	nitrilotriacetic acid	1.3E-02	6293.03
	manganese sulfate	6.3E-03	3146.51
	ferrous ammonium sulfate	5.0E-03	2517.21
	cobalt chloride	1.3E-03	629.30
	zinc sulfate	1.3E-03	629.30
	cupric chloride	1.3E-04	62.93
	nickel chloride	1.3E-04	62.93
	sodium molybdate	1.3E-04	62.93
	sodium selenate	1.3E-04	62.93
Cysteine-sulfide solution ³⁰	sodium tungstate	1.3E-04	62.93
	L-Cysteine·HCl·H ₂ O	7.1E-04	357.44
	Na ₂ S·9H ₂ O	7.1E-04	357.44

Table 15: Nutrient media chemical composition and annual consumption. *

MES=morpholinoethanesulfonic acid

Table 15 lists the needed chemicals and their concentrations for the nutrient medium supplied to the reactors. Assuming a medium flow of $57.47 \frac{m^3}{h}$, an annual 500,000 m^3 of nutrient solution is needed, which is translated into an annual consumption in L or kg per chemical.

Control systems such as anti-foam systems, acid, and base control systems, are the only known additional auxiliary streams for the growth and production reactors. It is known that both acid and base streams use 2M KOH or HCl streams, but as such systems do not supply continuous streams to the reactor, but rather act on demand, their inflows are not calculated. Antifoam 204 is available for emergency foam control, but is already in the nutrient feed, and is typically not needed. Its stream is therefore not calculated either²².

Syngas processing

The waste gas from the steel mill cannot be used directly for fermentation. To have the highest possible conversion, efficiency and productivity for the production of ethanol the gas must be processed. Therefore a gas processing section is designed for removal of the impurities. Next to removal of impurities the gas must also have a composition close to the ideal stoichiometric order for fermentation. This will improve conversion, efficiency and productivity. The ideal composition for fermentation can be seen in **Table 16**. This shows that all impurities and more than half of hydrogen must be removed, while 2180.61 mol/s of CO should be formed. To accomplish this several specialized sections are designed, each responsible for removing different impurities.

Carbon based solids

The first section is chosen to be responsible for carbon based solid removal. Removal of solids is a logical first step, because solids may clog equipment. This will definitely give problems later on. The solids are removed by cyclones (S-1). This equipment type is chosen, because it is easy to maintain. There are no moving parts present, hence little change of failure. A cyclone can also operate fine with the initial conditions (20°C and 1 bar). The conditions do not have to be changed for the separation to occur. This is another reason why solid removal is done first.

Compound	Target (mol/s)	Present in raw gas(mol/s)	To be removed(mol/s)
NO	0	19.01	19.01
SO ₂	0	8.90	8.90
CO	5846.01	3665.40	-2180.61
CO ₂	0	1088.68	1088.68
H ₂	11427.51	25465.16	14037.65
H ₂ O	0	31.66	31.66
NH ₃	0	33.49	33.49
CH ₄	0	1006.62	1006.62
Tar	0	4.45	4.45
N ₂	0	4275.83	4275.83
H ₂ s	0	16.74	16.74
Char, ash, other solids	0	4.40E-06	4.40E-06

Table 16: target composition

Tar removal

The second step is to remove tar. One assumption for the design was made: the tar is not sticky. This makes the design less complicated, because sticky compounds will likely clog the cyclones. If this would have been taking into account, then before the solid removal step the tar must be separated from the other compounds present in the gas. Another way could be to remove tar as first step. However to remove tar, a high temperature is needed. After tar removal the gas needs to be cooled down again so the cyclones do not melt due to the high temperature. And that would increase our energy costs.

The operation conditions for the removal of the tar is 1500°C and 10 bar. Firstly the gas is compressed to 10 bar (1.K-1). Compressing before heating is desired, because a higher temperature will result in a higher volume. You would need more energy to compress a higher volume resulting in higher costs. After compressing the gas needs to be cooled down (E-1) to function as a coolant for the streams for other sections (1.E-2, 1.E-3). During the cooling down of the other gas streams the gas is heated up. To further increase and maintain the desired temperature a furnace (1.E-4) is used. The reactions take place in a tar reformer(1.V-1), see **Equation 21**. A high temperature vessel where tar compounds react with water forming carbon monoxide and hydrogen. An advantage of this reaction vessel is that not only tar is converted,

but methane undergoes a similar reaction.³¹ At high temperature ammonia becomes unstable and decomposes to nitrogen and hydrogen.³²

- $C_{10}H_8 + 10 H_2O \rightarrow 10 CO + 14 H_2$
- $CH_4 + H_2O \rightarrow CO + 3 H_2$
- $CO + H_2O \rightarrow CO_2 + H_2$
- $CH_4 + CO_2 \rightarrow 2 CO + 2 H_2$
- $2 NH_3 \rightarrow 3 H_2 + N_2$

Equation 21: Tar, methane and ammonia conversion

Hydrogen sulfide removal

After the gas is purified from tars, methane and ammonia the gas leaving the reactor must be cooled down. This is done by a heat exchanger (E-3) which was mentioned in the previous section. The raw gas feed cools down the hot gas from the reactor until it reaches 650-760°C.³² The removal of hydrogen sulfide takes place in a fixed bed reactor(1.V-2a/b) at approximately 10 bar. The real pressure may be lower due to pressure drop in the pipelines, however pressure does not have a big effect on reaction efficiency. The bed consists of zinc titanate (zinc titanium oxide). Zinc titanates are able to decrease the H₂S concentration to less than 10 ppm. The TiO_x group protects the Zn ions from reduction by H₂ and CO. This allows Zinc titanates to work at higher temperatures than ZnO.³²

The fixed bed reactor operates in three stages. The first stage is the absorption of H₂S see **Equation 22**. This will convert ZnO to ZnS. When there is no more ZnO left, then H₂S cannot be absorbed anymore. The feed gas will then go to the second reactor. Meanwhile the first reactor is in the regeneration stage. The first reactor is closed off from the feed gas while oxygen is provided for regenerating ZnS back to ZnO, see **Equation 22**. After all ZnO is regenerated the reactor will be in stage 3. The reactor will then be flushed with nitrogen to remove all the oxygen from the reactor. Oxygen is not a desirable compound to have in the gas stream, because *Clostridium Ljungdahli* is not very resistant to oxygen. In addition to oxygen SO₂ will also be purged. To safely dispose the purged gas mixture SO₂ has to be neutralized. The purged gas will go to a vessel (1.V-5) where sulfuric acid is formed from SO₂, O₂ and

cooling water from a later step. Simultaneously the mixture is neutralized with a 1M NaOH solution(1.T-2, 1.P-3a/b).

- $ZnO + H_2S \rightarrow ZnS + H_2O$
- $2 ZnS + 3 O_2 \rightarrow 2 ZnO + 2 SO_2$

Equation 22: Hydrogen sulfide absorption and zinc oxide regeneration

NO and SO₂ removal

The removal of NO and SO₂ takes place in a CSTR (1.V-3). The operating conditions are 35-50°C and 1 bar.³³ The gas outlet from the fixed bed reactors is cooled down in a heat exchanger (1.E-2) by the gas after compression. SO₂ and NO₂ are by themselves not soluble in water. To remove these compounds a conversion must take place to make them soluble. Dissolving NO and SO₂ is possible by absorption in a KMnO₄ and NaOH solution. KMnO₄ will react with SO₂ forming SO_x ions, while NaOH will react with NO forming NO_x ions. These are not the only products, some side products will also be formed, see **Equation 23**.³³

- $NO + MnO_4^- + 2 OH^- \rightarrow NO^{2-} + MnO_4^{2-} + H_2O$
- $NO^{2-} + 2 MnO_4^- + 2 OH^- \rightarrow NO_3^- + 2 MnO_4^{2-} + H_2O$
- $3 NO_2^- + 2 MnO_4^- + H_2O \rightarrow 3 NO_3^- + 2 MnO_2 + 2 OH^-$
- $NO + MnO_4^- \rightarrow NO_3^- + MnO_2$
- $SO_2 + H_2O \rightarrow 2 H^+ + SO_3^{2-}$
- $H^+ + OH^- \rightarrow H_2O$
- $2 MnO_4^- + SO_3^{2-} + 2 OH^- \rightarrow 2 MnO_4^{2-} + SO_4^{2-} + H_2O$

Equation 23: NO and SO₂ conversion and side reactions

A disadvantage of this technique is that recycling the whole waste stream is not an option due to the conversion of NO and SO₂ to NO₃⁻ and SO₄²⁻. The high concentration of OH⁻ and MnO₄⁻ coming in reduces the regeneration of NO₂ and SO₂. Regeneration is possible by reducing the inlet flow of OH⁻ and MnO₄⁻. This shifts the equilibrium more to the left, regenerating OH⁻ and MnO₄⁻. If the concentration of OH⁻ and MnO₄⁻ becomes too low, then the fraction of solution must be purged, while more OH⁻ and MnO₄⁻ are pumped in the reactor.

Nitrogen removal

The final step in the process is the removal of nitrogen. This removal is done by nitrogen membrane filters. There are three requirements for successful removal of nitrogen by membrane filters. The first is the inlet pressure. There needs to be a specific inlet pressure to push the gas through the membrane filter. The next requirement is the inlet temperature. The membrane filter is not tolerable to all temperatures, due to the membrane material. The last requirement is that no water droplets must be present in the gas. Water droplets may block the membrane and cause failure.

First the gas is compressed to the desired inlet pressure of 10 bar (1.K-2). Compression will increase the temperature of the gas significantly. A logical next step is cooling the gas in a heat exchanger with water (1.E-5). The cooling water leaving the heat exchanger is used in the SO₂ neutralization step, mentioned in the “Hydrogen sulfide removal” section. The heat exchanger may form water condensate in the gas. Water droplet may also be already present in the gas from the CSTR. Finally the water droplet are removed by a demister (1.S-2). The gas will go through the filter, while the water droplet are blocked and dropped down. Now the gas is ready to pass through the membrane filters and remove nitrogen. A fraction of the removed nitrogen is stored in a vessel (1.V-4) at 20 bar. The stored nitrogen is used when the plant shuts down when there is no more nitrogen inflow. To maintain this pressure a small compressor compresses a fraction of the nitrogen coming in. This storage will supply the plant’s nitrogen needs, e.g. flushing the fixed bed reactors.

Syngas process modeling

As previously discussed the gas processing section consists of many different equipment. To determine the specifications and if the impurities could be removed most of the process was modeled, see **Figure 5**. The equipment that was not modeled are the storage tanks/vessels, pumps and filters. It was not necessary to model these type of equipment, because their specifications could be determined by literature and calculations by hand, see section Equipment Specifications.

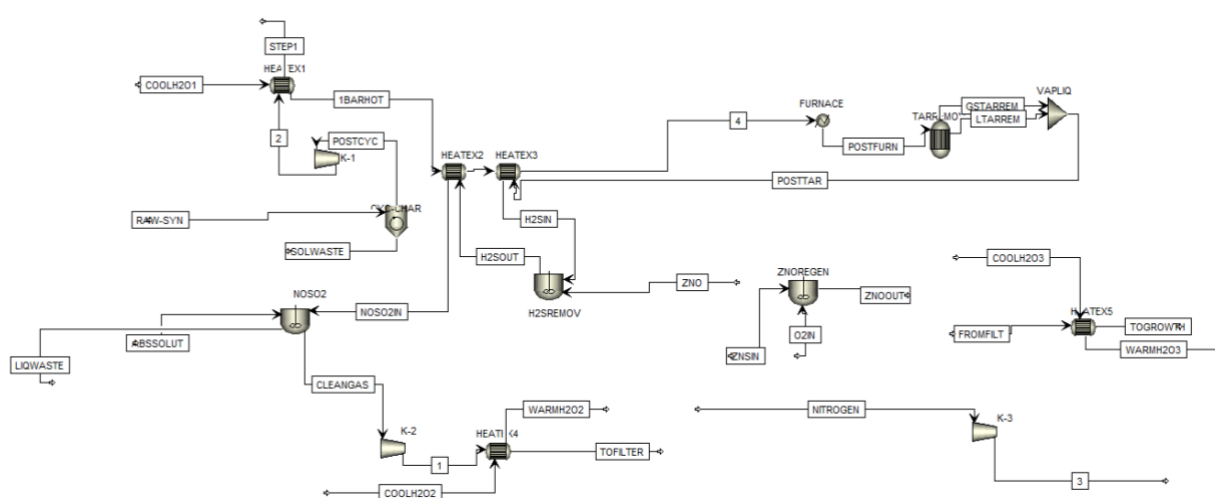


Figure 5: syngas processing Aspen model

Raw gas feed

As previously stated the total waste gas from the steel mill is 10.8 ton/h. All compounds and impurities were put in as mass fractions. Tars can be of different sizes and compositions. In this model naphthalene was taken as tar, due to tar consisting of 10 wt% naphthalene.³⁴ To simulate solid particles, e.g. char and ash, carbon was taken as solid. A Particle Size Distribution was calculated with the normal distribution function. D50, the median diameter, was specified as 500 micron with a standard deviation of 100 micron.

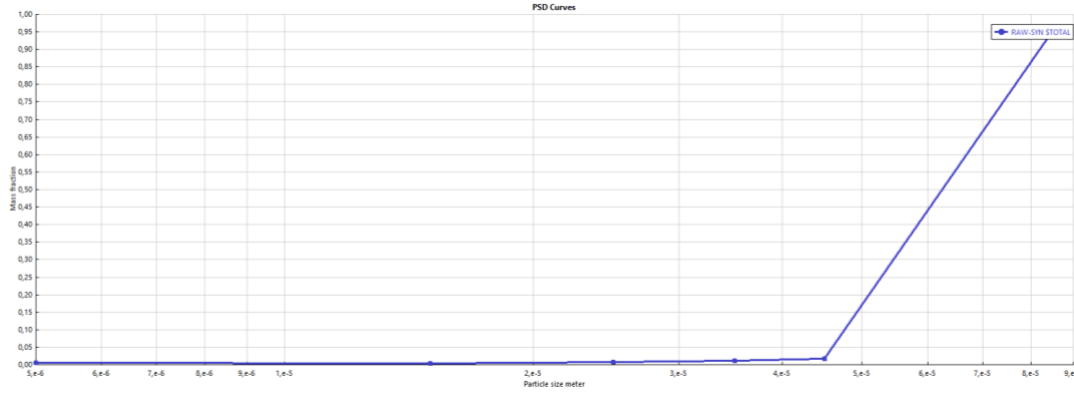


Figure 6: Solid carbon mass fraction plot

Cyclone

The cyclone was modeled using the Leith-Licht calculation method with type Stairmand-HT. The Leith-Licht calculation method describes particle motion in the entry and the collection regions using an equation of particle motion. It makes several assumptions for simplifying the equations of particle motion

- Gas path lines are taken as circles in the vortex.
- The angular velocities are everywhere equal giving rise to a radial slip.
- The radial slip gives rise to a radial drag force, acting towards the axis.
- The radial acceleration of a particle is negligible, thus making the drag force equal to the mass of the particle times its centripetal acceleration.

The radial migration velocity of a particle is described by the following equation.

$$\frac{dR}{dt} = \frac{d_p^2 \rho_p}{18\mu} \frac{u_{t2}^2 R_2^{2n}}{R^{2n+1}}$$

Where the particle of diameter d_p and density ρ_p in question is at radius R after spending time t within the cyclone.³⁵

According to the simulation the amount of solid in the gas stream had no influence on the efficiency. Choosing the Stairmand-HT type the efficiency remains constant at 99.5%. If the number of cyclones simulated in parallel is decreased, then the inlet gas velocity would exceed the correlation velocity limit resulting in an error. This is a logical error, because a parallel setup will spread the gas flow over more cyclones resulting in a lower flow rate and inlet velocity per cyclone. It was found that the simulation worked perfectly by specifying 500

parallel cyclones . The diameter is chosen to be 0.5m. By keeping the diameter low more cyclones can be put in one area compared to cyclones with a higher diameter. This increases the amount of carbon separated per unit area. The area of the plant would then be used more efficiently.

Compressors

All compressors were assumed as being isentropic. The discharge pressure was specified to the desired pressure for the next step in the process. As discussed previously compressor 1.K-3 only compresses a fraction of the total removed nitrogen from the filter. For simulation this value was taken as 1000 kmol/h. This is a rather broad estimation, as only 100 kmol/h oxygen enters the fixed bed reactor and most of the oxygen will be converted.

Heat exchangers

The heat exchangers are modeled by specifying the hot stream outlet temperature as all heat exchangers function as coolers for the gas stream of interest. The U value was assumed to be 200 Watt/m²*K. Three heat exchangers, 1.E-1, 1.E-5 and 1.E-6, use 100000, 70000 and 50000 kmol/h cooling water respectively to cool down the gas stream. The cooling water temperature was set up as 20 °C. Water was chosen as cooling medium over air, because water has a higher heat capacity. During heat exchange steam is formed which can be used for the distillation set up.

Tar reformer

An equilibrium reactor was chosen as the model for the tar reformer, because the reactions that take place in the reactor are equilibrium reactions. It was found that the minimum temperature for close to 100% conversion of tar, methane and ammonia at 10 bar is 1500 °C. The reactions simulated in the equilibrium reactor are discussed previously.

In reality there might be more reactions taking place due to great variety of compounds in the reactor. For simplicity sake only the main reactions were simulated as the function of the model was to simulate the removal of tar, ammonia and methane. The equilibrium reactor model requires a vapor and liquid stream. However in this process no liquid is present. To bring the two streams back to one, the vapor and liquid outlet streams are combined by a mixer.

Fixed bed reactors

The fixed bed reactors were modeled as a CISTR at 700 °C and 10 bar to find out how much ZnO per hour is needed for removing H₂S. The reactor model specifications were irrelevant. The equipment specifications were determined by calculation (see **Fixed bed reactor**). A similar procedure was done for the regeneration stage. The CISTR was modeled as stand-alone, because the regeneration stage is separate from the overall gas stream in the process. The only function of the stand-alone CISTR is to determine the amount of oxygen per hour necessary for complete regeneration.

The zinc oxide and zinc sulfide were taken as solids with a calculated normal particle size distribution of 0.05 and 0.01 micron for D50 and the standard deviation respectively.

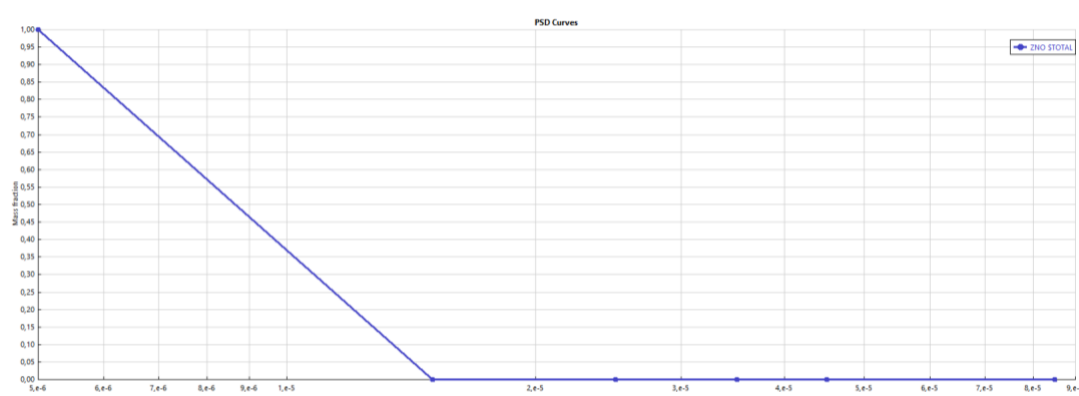


Figure 7: : Zinc oxide mass fraction plot

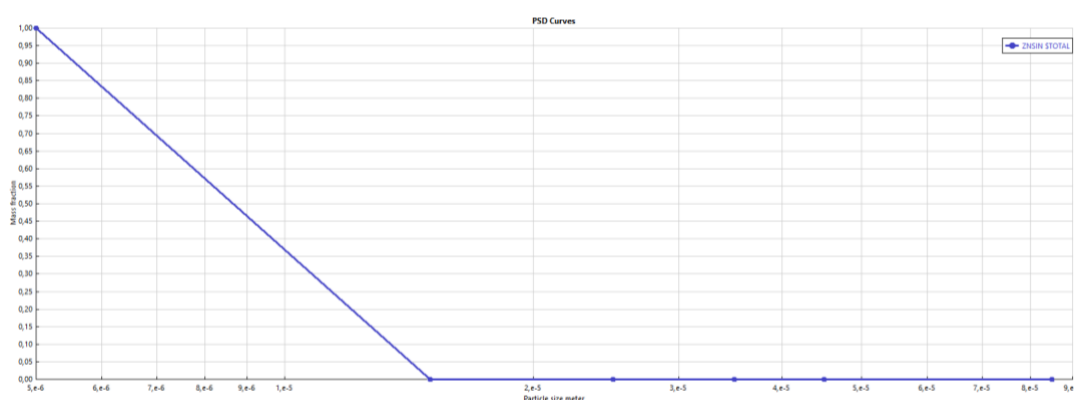


Figure 8: Zinc sulfide mass fraction plot

CSTR

A CISTR model was used to simulate the nitric oxide and sulfur dioxide absorption reactor. The CISTR was set up with a temperature of 35°C, 1 bar and a reactor volume of 2310m³. The calculation of the volume is calculated in section **CSTR**. The inlet flow of the absorption solution was taken as 100 kmol/h K⁺ and MnO₄⁻ and 1000 kmol/h Na⁺ and OH⁻ with 1000 kmol/h water to represent the pumped liquid.

Results

As can be seen by comparing **Table 16** and **Table 17** nearly all impurities are completely removed. However there is now even more hydrogen in the gas as before. The extra hydrogen is formed from the conversion of tar and methane in the tar reformer. Removing the excess hydrogen, which is a huge amount, can be very dangerous. If hydrogen is removed by a filter, then it must still be neutralized to prevent an explosion. Another way could be to burn the hydrogen in a vessel. Again this can be very dangerous and difficult to contain safely.

Compound	Target (mol/s)	Achieved(mol/s)	Difference(mol/s)	Original(mol/s)
NO	0	1.36E-06	1.36E-06	19.01
SO ₂	0	8.71E-15	8.71E-15	8.90
CO	5846.01	5846.00	-0.01	3665.40
CO ₂	0	2.04	2.04	1088.68
H ₂	11427.51	27638.82	16211.31	25465.16
H ₂ O	0	17.35	17.35	31.66
NH ₃	0	0.51	0.51	33.49
CH ₄	0	17.11	17.11	1006.62
Tar	0	0.00	0.00	4.45
N ₂	0	0.08	0.08	4275.83
H ₂ S	0	0.07	0.07	16.74
Char, ash, other solids	0	0.00	0.00	4.40E-06

Table 17: Achieved gas composition

Reactor Model

As previously explained, the reactor section of the process designed consisted of two primary reactors, reminiscent of a two-stage continuous process of the pilot scale plant, of which the design was scaled up from, and which procedure has been explained thoroughly in preceding sections. In addition to the scale-up calculations showed to have been modeled in a Microsoft Excel spreadsheet, the two reactors, consisted of a growth/acidogenesis reactor (R1) and a production/solventogenesis reactor (R2), were also modeled in Aspen Plus V.8.6 to further confirm the validity of the scale-up.

Through the upcoming sections, the modeling process and results for both R1 and R2 are elaborated on. It should be noted that all simulations pertaining to both reactors performed using the NRTL-RK method. Furthermore, since both reactors were modeled using the RStoic block, a fractional conversion of a reference reactant is required for each of the reaction to quantify the extent of reaction/conversion of the feed and also the reaction selectivity. The fractional conversion, by definition, can be written as the expression shown in **Equation 24**. The specific fractional conversion for each of the reactions in **Equation 3 - Equation 6** for each of the reactors will be calculated and elaborated further within their subsequent sections.

Equation 24 Fractional conversion of A =
$$\frac{\text{mol of A converted by the reaction}}{\text{total mol of A present in the feed}}$$

Growth/acidogenesis reactor (R1)

The first stage, in accordance to that of the pilot plant, aims to reach a product ratio of 13:1 acetate-to-ethanol ratio. As shown in **Table 18**, the fractional conversion values for each of the reactions were calculated based on the amount of mole flow being converted and the total amount of mole flow in the feed, both of which were obtained from the previously explained absorption factor productivity scale-up, and the gas inflow splitting, respectively. The fractional conversion was calculated for a given reference component, for each reaction, which in this case is either CO or CO₂ based. It should be noted that the fractional conversion can be seen to reflect a selectivity ratio of 11.5:1 acetate-to-ethanol, and not 13:1, which is tied to the inherent absorption factor of each of the gases in the process itself. In other words, to achieve an outlet product ratio of 13:1 acetate-to-ethanol, a selectivity ratio of 11.5:1 is a requirement.

Reactions	Flow converted (mol/s)	Flow in the feed (mol/s)	Fractional conversion
$6\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 4\text{CO}_2$	79.40	944.86	0.08
$2\text{CO}_2 + 6\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O}$	0.03	0.32	0.08
$4\text{CO} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2\text{CO}_2$	865.46	944.86	0.92
$2\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}$	0.3	0.32	0.92

Table 18. Fractional conversion calculation for R1 Aspen Plus V8.6 model

As shown in **Figure 9**, the real R1 was attempted to be modeled using 3 virtual blocks in Aspen Plus V.8.6, namely R1,GRW1; R1,GRW2; and R1,FLASH. The said reactor, therefore, has overall 2 feed streams and 2 outlet streams, one each for gas and liquid. It should also be noted that the gas feed stream R1,G,IN, based on the gas flow splitting showed earlier in **Table 8**, consists of an entire gas feed for a parallel design proposed earlier with 5 sets of reactors. Therefore, to only model a single set of reactors, a multiplier block with a factor of 0.2 was added to further split the total gas feed stream by 5, thus only passing a gas stream of 1 set of reactors into the R1 model. For the liquid feed, consisting of only water in the model to simulate a flow rate of both nutrient and water stream in the real first stage reactor, which therefore amounts to a 977.03 m³/h flow rate, matching the previously explained dilution rate-based liquid flowrate scaling.

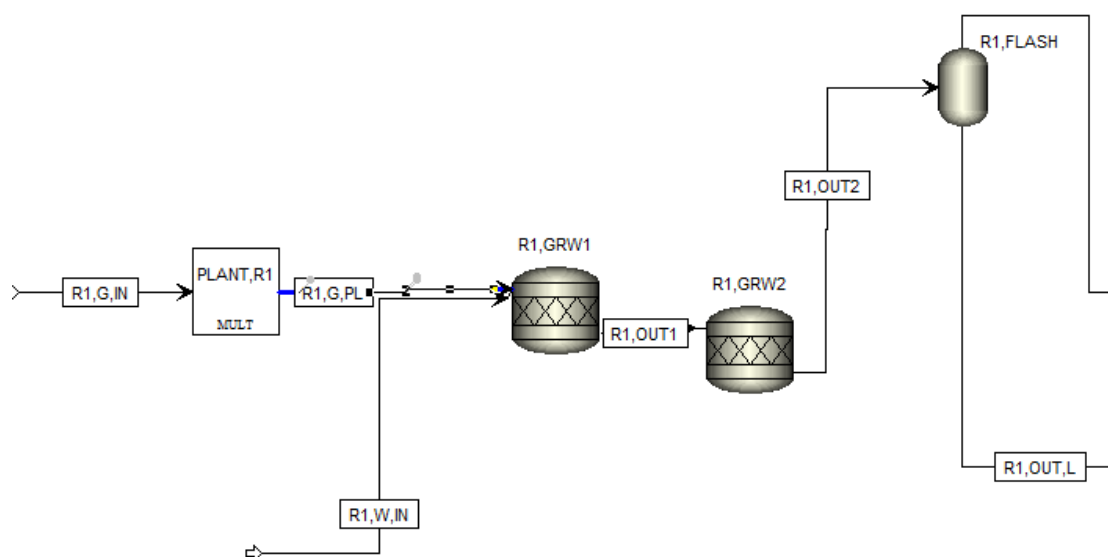


Figure 9. R1 Aspen Plus V8.6 model

As for the two reactors, R1,GRW1 and R1,GRW2, they are both modeled to be identical to each other, having exactly the same set of 4 stoichiometric reaction equations (**Equation 3 - Equation 6**), with their corresponding reaction enthalpy and fractional conversion as tabulated in **Table 18** above. Both reactor blocks operate at a temperature of 35°C and a pressure of 10 bar, as specified in the previous sections pertaining to the scale-up and pressure-based enhancement of productivity. The reasoning behind the use of two reactor blocks to model a real R1 is due to the fact that in reactions shown in **Equation 3** and **Equation 5**, aside from the formation of the main metabolites, the reaction also released CO₂, which also is a reactant for the reactions shown in **Equation 4** and **Equation 6**. While R1,GRW1 would have converted the reactants in the entire feed stream of R1,G,PL, the second block, R1,GRW2 was there to convert the reactants in the outlet stream of R1,GRW1 into products. As for the flasher block R1,FLASH, it was set to not perform any form of cooling or compression, implying that it was specified to work at the same temperature and pressure with the reactor blocks, and would simply split the outlet stream of R1,GRW2 according to their phase, vapor or liquid.

The calculation run, along with some of the results can be seen in **Figure 10**. It should be noted that a simple heat exchanger block, R1CAP, had to be added to perform a preliminary calculation on handling the heat output of the reactions, which in the case of R1, can be seen to amount to approximately 30MW of heat. It is worth noting that the aforementioned duty was calculated based on the values found on the reaction enthalpy as listed in **Equation 3 - Equation 6**. It might therefore be the case where the exact heat production term will have to be measured by the means of calorimetry, for the specific growth rate, cell concentration, and substrate used in the design. The block R1CAP was specified based on the cooling duty it needs to fulfill, operating at the same pressure as the reactors, with an inlet stream of water at 18°C. The resulting requirement in cold water flow rate, which is 1400 metric tons/hr, and a temperature difference of 17°C, will then be utilized later on in designing the specification of the cooling equipment. An apparent observation can be immediately made on the stream R1,OUT,G, which shows an effectively empty gas stream. While this is partly caused by the use of a feed that is designed to be in a stoichiometric amount, this occurrence is also caused by the excessive gas solubility modeled by the NRTL-RK method. This issue, however, can be easily corrected by using the proper Henry's constant as an input to the model. While unrealistic, the complete void of the gas stream in the case of R1,OUT,G can be seen to be of negligible influence as nevertheless, all of the reactive gases have indeed reacted to completion, as indicated by the stream results for R1,OUT,L tabulated in **Table 19**. Furthermore, from

Table 19, it can be seen that the product ratio between acetate and ethanol, is indeed approximately 13:1, as estimated by the previously described Microsoft Excel-based model. Finally, it is also evident that the concentration of acetate, being the primary metabolite in the case of R1, is indeed found to be about 1.8 vol%, which is well below the previously assumed 10 vol% threshold values.

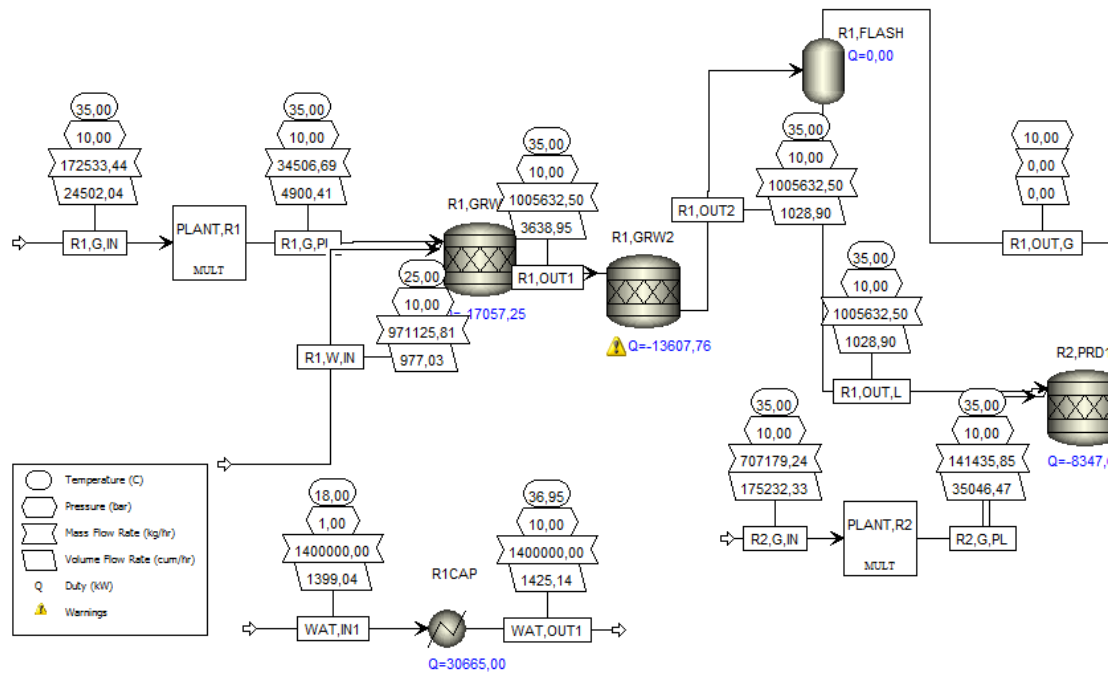


Figure 10. R1 Aspen Plus V8.6 model with results and addition

Component	Flow (kmol/hr)
H ₂	0
CO ₂	1.14E-07
CO	0
CH ₄	1.98
N ₂	497.59
Ethanol	24.23
H ₂ O	53930.1
Acetate	316.04

Table 19. R1,OUT,L stream results

Production/solventogenesis reactor (R2)

The second stage, in contrast to that of the pilot plant, aims to reach a product ratio of 20:1 ethanol-to-acetate ratio. The significantly higher product ratio is based on the highest ratio found upon the examination of numerous literature on production/solventogenesis reactor³⁶. As shown in **Table 20**, the fractional conversion values for each of the reactions were calculated similarly to that of the first stage, with values also obtained from the previously explained absorption factor productivity scale-up, and the gas inflow splitting. The fractional conversion was calculated for a given reference component, for each reaction, which in this case is either CO or CO₂ based. An additional reaction, however, shown as **Equation 25**, is required to properly model R2 and achieve the aforementioned product ratio. **Equation 25** essentially included a pathway in converting acetate produced in the first stage into ethanol, in achieving the aforementioned product ratio. This is required as without either partial or complete conversion of the acetate being produced in the first stage into ethanol, carbon balance-wise, it is by definition impossible for the second stage to achieve the target product ratio. While ideally the additional reaction would also have to be modulated by a selectivity factor and efficiency factor in determining its fractional conversion, for the sake of simplification of the model, the said additional reaction was set at a fractional conversion value of 1, with acetate being the reference reactant, implying that all of the acetate being produced in the first stage will be completely converted into ethanol in the second stage. Arguably, the simplification described earlier can be said to be justifiable as essentially the described complete conversion of acetate from the first stage to ethanol step is nothing more than a virtual micro pathway inside the overall model of R2. Based on this reasoning, it can be said that regardless of how the reactions inside of R2 were being modeled and arranged, the overall result of the model should remain unaffected. It should also be noted that in the case of **Equation 25**, the enthalpy of the reaction is purposely left unaccounted due to its insignificance relative to the rest of the process.



Reactions	Flow converted (mol/s)	Flow in the feed (mol/s)	Fractional conversion
$6\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 4\text{CO}_2$	4667.76	4901.15	0.95
$2\text{CO}_2 + 6\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O}$	1.6	1.68	0.95
$4\text{CO} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2\text{CO}_2$	233.39	4901.15	0.05
$2\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}$	0.08	1.68	0.05
$\text{CH}_3\text{COOH} + 2\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O}$	-	-	1

Table 20. Fractional conversion calculation for R2 Aspen Plus V8.6 model

As shown in **Figure 11**, the real R2 was attempted to be modeled using 4 virtual blocks in Aspen Plus V.8.6, namely R2,PRD1; R2,PRD2; R2,PRD3; and R2,FLASH. The said reactor, therefore, has also 2 feed streams and 2 outlet streams, one each for gas and liquid. Again, much like R1, the gas feed stream R2,G,IN is based on the gas flow splitting showed earlier in **Table 8**. As the gas feed stream R2,G,IN also consists of an entire gas feed for a parallel design proposed earlier with 5 sets of reactors, to only model a single set of reactors, a multiplier block with a factor of 0.2 was added to further split the total gas feed stream by 5. For the liquid feed, in the case of R2, in terms of both composition and flow rate, is entirely dependent on the liquid outlet stream from R1, namely R1,OUT,L.

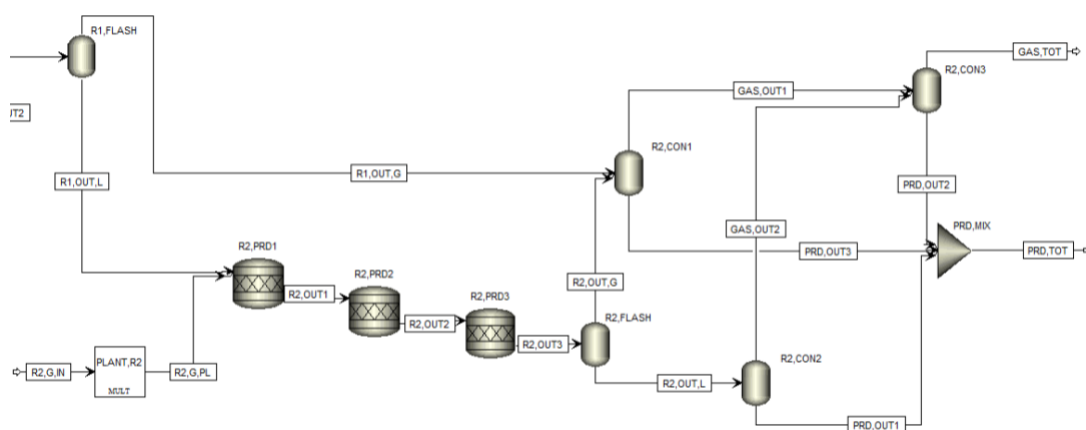


Figure 11. R2 Aspen Plus V8.6 model

For the three reactors blocks, the last two blocks, R2,PRD2 and R2,PRD3, much like the two reactor blocks in R1, and also for the same reasoning, are both modeled to be identical to each other, having exactly the same set of 4 stoichiometric reaction equations (**Equation 3 - Equation 6**), along with their corresponding reaction enthalpy and fractional conversion shown in **Table 20**. Both reactor blocks also operate at a temperature of 35°C and a pressure of 10 bar. As for the additional reactor block, R2,PRD1, it is modeled with only one stoichiometric reaction equation, that is **Equation 25**, using a fractional conversion of 1 for the reasoning explained earlier, simply to achieve the conversion of all acetate contained in the R1,OUT,L stream into ethanol before the 2 following reactor blocks, R2,PRD2 and R2,PRD3, convert the gases into the desired products. The flasher block R2,FLASH, also works in the same way as it was in R1 since it was set to perform nothing but splitting the outlet stream of R2,PRD3 based on them being of liquid or vapor.

Additionally, a number of flasher blocks were also added to the model, namely the blocks R2,CON1; R2,CON2; and R2,CON3. The flashers R2,CON1 and R2,CON2 are both mainly serves to depressurize the fluid, gas in the case of R2,CON1, and liquid in the case of R2,CON2, from 10 bar of operating pressure to atmospheric pressure of 1 bar. On top of that, the flasher R2,CON1, which takes the gas outlet stream of both reactor models, R1,OUT,G and R2,OUT,G, also act as a slight condenser as it was set to operate at a temperature of 20°C, lower than the 35°C temperature of the gas outlets. As for the flasher R2,CON3, it serves a purpose mainly as a condenser since it was set to operate at 10°C, to now condense as many of the primary products, which are ethanol and acetate, along with some water vapor, out of the now atmospheric gas stream from R2,CON1.

The calculation run, along with some of the results can be seen in **Figure 12**. It should be noted that, again, similar to that of R2, a simple heat exchanger block, R2CAP, had to be added to perform a preliminary calculation on the handling of the heat output of the reactions, which in the case of R2, amounted to approximately 400MW of heat. It is also worth noting that the aforementioned duty was calculated based on the same values found on the reaction enthalpy as listed in **Equation 3 - Equation 6**. Since R2 operates at a significantly different condition with respect to R1, it only make sense for the exact heat production term to be re-measured by the means of calorimetry, for the specific growth rate, cell concentration, and substrate used pertaining to R2. Much like R1, the block R2CAP was specified based on the aforementioned cooling duty it needs to fulfill, operating also at the same pressure as the reactors, with an inlet stream of water at 18°C. The resulting requirement in cold water flow rate of 18000 metric

tons/hr and the temperature difference of 17°C will then be utilized later on in the specification of the cooling equipment for the reactor.

While the R2 model also suffers from the same issue as R1, which is caused by the excessive gas solubility modeled by the NRTL-RK method, both the reactor gas outlet stream, R2,OUT,G, and the total gas outlet stream GAS,TOT, can be seen to not be completely void of material. The exact composition for both of the aforementioned gas streams can be found tabulated in **Table 21**. It is important to note that by looking at the composition of the gas streams, almost all of the primary products were able to be recovered into the liquid phase for further processing. This then raises a point of concern on whether or not any of the condenser blocks were worth adding at all, considering the very minute amount of product it will be able to recover. The design kept the condenser blocks while keeping in mind that the very well recovered products might have also been an effect of the same issue with using NRTL-RK without properly changing the Henry's constant. Furthermore, it can also be seen that almost all of the reactive gases have indeed reacted to completion, with the exception of a small amount (~1.58 mol% of the feed R2,G,PL) of excess H₂ leftover. Lastly, it is worth mentioning that since the design for the reactors specifically assumes an inflow composition relatively early in the design process, the gas, unlike that of the processed gas from the syngas processing section, is not completely void of N₂.

As for the liquid streams, namely R2,OUT,L, and the total liquid outlet stream PRD,TOT, both can be seen to also contain virtually none of the reactive gases left. Furthermore, from **Table 21**, it can be seen that the product ratio between ethanol and acetate, is indeed approximately 20:1, as estimated by the previously described Microsoft Excel-based model. Finally, it is also evident that the concentration of ethanol, being the primary metabolite in the case of R2, is indeed found to be about 12 vol%, which while higher, is still fairly close to the assumed 10 vol% threshold value. It is also worth noting that while in the present model, the concentration of almost all of the components in the two liquid streams R2,OUT,L and PRD,TOT can be seen to be practically identical, this could also be an implication of the uncorrected Henry's constant for the NRTL-RK method. Fixing the said parameter could potentially increase the quantity of the products in the gaseous streams, implying that the effect of having a condenser might prevail more relative to the current reported model.

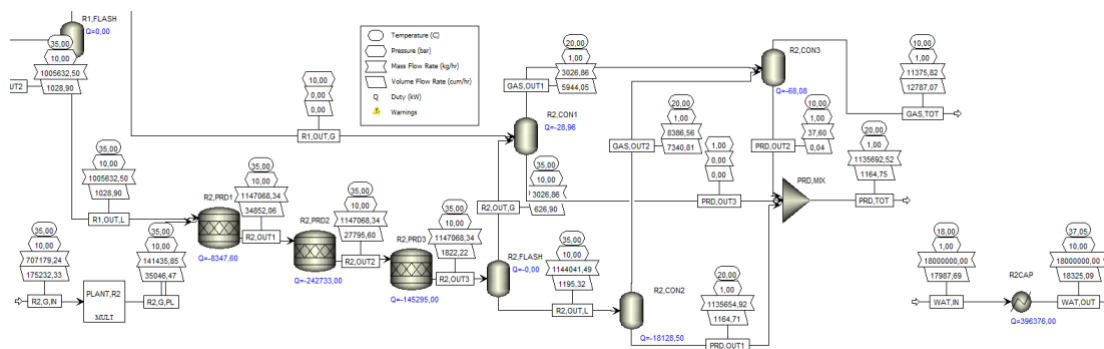


Figure 12. R2 Aspen Plus V8.6 model with results and addition

Component	Flow (kmol/hr)			
	R2,OUT,G	GAS,TOT	R2,OUT,L	PRD,TOT
H ₂	145.97	145.97	1.45E-03	6.85E-08
CO ₂	0	0	0	0
CO	0	0	0	0
CH ₄	0.35	3.44	14.26	11.17
N ₂	95.55	384.07	433.81	145.29
Ethanol	0.55	1.13	2392.46	2391.89
H ₂ O	1.37	0.81	56299	56299.6
Acetate	1.74E-03	5.4E-04	119.87	119.87

Table 21. R2 stream results

Product Work-up

Extractive distillation³⁷

There are no sources in the current document.

The design objective is to obtain ethanol with a purity of at least 99%. To achieve this purity, regular fractional distillation is not sufficient, as water and ethanol form an azeotrope at approximately 95%. Several methods are applied in industry that can achieve this. In this project the choice was made for extractive distillation, which is widely used in industry for this purpose. Arguments for the usage of this separation method include its high product purity and low energy consumption and capital investment costs.

Extractive distillation works by adding a solvent to the distillation column. The solvent changes the relative volatility of the key components, in this case water and ethanol. This enables the separation of ethanol with very high purity. The solvent has to possess a number of properties:

no new azeotropes can be formed in the mixture, the solvent has to be completely miscible and it has to be the highest boiling component in the mixture. In the case of an ethanol/water mixture, ethylene glycol is a very suitable solvent that is broadly used for this mixture in industry.

Extractive distillation is carried out in a two feed distillation column, where the solvent is added near the top of the column, to ensure a presence throughout the column. The solvent feed cannot be at the very top of the column, because then the ethanol vapor can carry the solvent to the distillate, which decreases the product purity. The mixture is feed near the bottom of the column, to ensure a high contact time between the mixture and the solvent, to achieve high purity.

For extractive distillation to work, the mixture has to be fed at near azeotropic concentration of ethanol. To ensure this, the feed to the extractive distillation column has to be pre-treated to achieve this concentration. The final step in extractive distillation is the recovery of the solvent. The fact that the solvent does not form any additional azeotropes makes for an easy separation of the solvent in a conventional fractional distillation column. The separated solvent can subsequently be reused in the extractive distillation column.

Product work-up feed

The feed for the product work-up is the flow coming from the reactor section. This also means that the work-up section is modeled for a fifth of the total gas feed. However, the nitrogen and methane concentrations were significantly higher compared to the solubility in water, which made the purification overly complicated and inefficient. These concentrations are caused by the modelling method used (NRTL-RK). For this reason the assumption was made that the nitrogen and methane concentrations were equal to the solubility values in water.³⁸ The feed original feed composition and the composition corrected with the above assumption can be found in **Table 22**.

compound	original composition (kg/h)	corrected composition (kg/h)
water	1004670	1004670
ethanol	92115	92115
acetate	7198	7198
hydrogen	1,41E-05	1,41E-05
nitrogen	4029,6	19,05
methane	178,5	23,10

Table 22: Feed composition of work-up section

Process design

The designing of the work-up process was mainly done in Aspen Plus. The aspen model is shown in **Figure 18**, the process parameters are in **Table 23**. All Aspen simulations were performed using the NRTL-RK method. This method models the liquid phase with the NRTL activity coefficient and models the vapor phase using the Redlich-Kwong equation of state. This model is applicable up to 10 bar, which is sufficient for this application. All distillation columns were modeled using a RadFrac block, a more rigorous method of simulation for distillation, which is also suitable for extractive distillation.

Initially three different columns were modeled. The first of these columns was used to prepare the feed by increasing the ethanol concentration to a value near the azeotropic concentration. The second column was the extractive distillation column, the final column was the solvent recovery column.

The specifications required to model an equilibrium based RadFrac model, the boilup ratio, the reflux ratio, the number of stages and the feed stage, were mostly finetuned by trial and error. Sensitivity analyses were used to find and confirm the optimal reflux ratio and boilup ratio. All columns were modelled with a pressure of 1 bar. Columns 1, 2 and 4 have a waste water stream, mainly consisting of water and acetate. These streams could be re-used in the reactor section, to prevent excessive waste production.

Feed preparation

It soon became clear that it was hard to make an efficient model for the preparation of the initial feed using just one column. The reason for this was the large difference in the feed concentration of ethanol compared to the concentration required for the extractive distillation. To accommodate for this, the preparation of the feed was modelled by two columns in series.

Column 1 (4.C-1)

The first column was used mainly to decrease the flow rate of the mixture to the second column, where the ethanol concentration was brought to near azeotropic conditions. This meant the energy consumption of the first column could be kept low, the reflux ratio and the boilup ratio were 1 and 0.5 respectively. The boilup ratio was found from the sensitivity analysis shown in **Figure 13**, at a ratio of 0.5 the ethanol fraction in the distillate is high enough for the second column, while keeping the loss of product in the bottoms as low as possible. The number of plates was set at ten, with the feed coming in at stage 8. Column 1 reduced the water and acetate content of the stream by approximately 85% and increased the ethanol weight fraction from 0.08 to 0.40. The model parameters were chosen to keep the ethanol lost in the bottoms.

To accommodate for the non-condensable gasses still present in the stream, mainly nitrogen and methane, a vent was installed on the reflux drum, which vented 0.1% of the distillate to the gas disposal system.

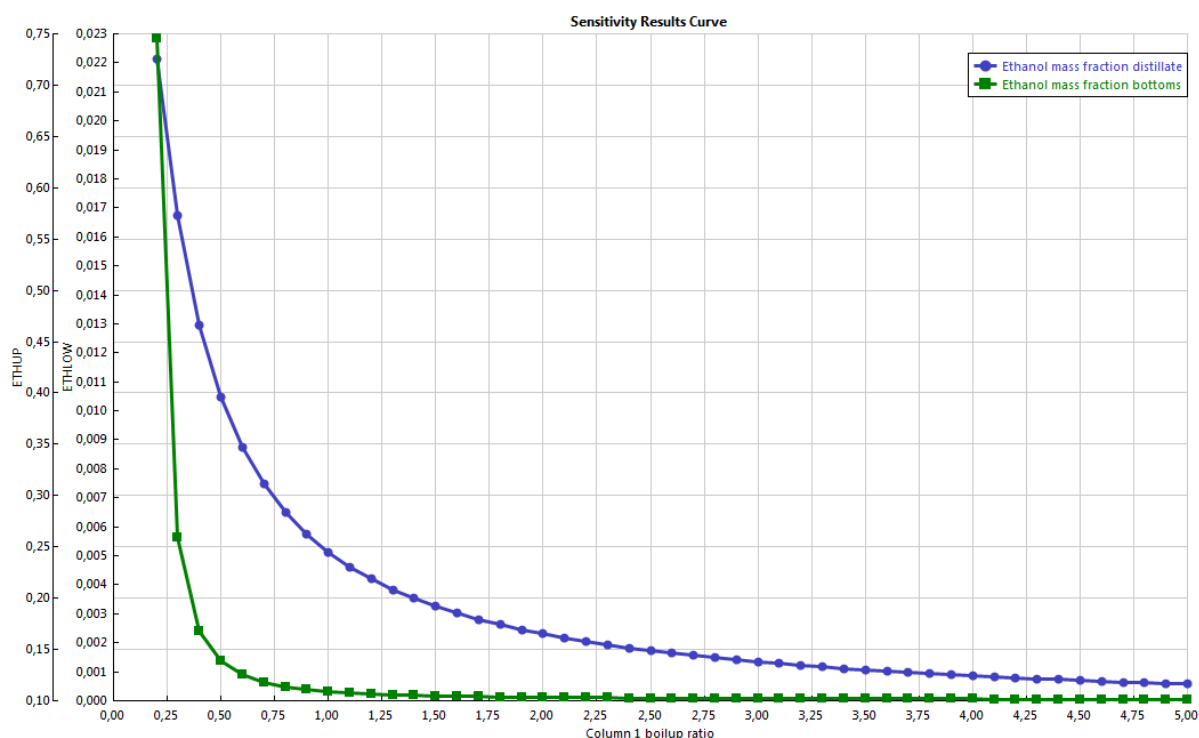


Figure 13: Column 1 boilup ratio sensitivity analysis

Column 2 (4.C-2)

As mentioned before, the second column was used to bring the ethanol concentration to near azeotropic conditions. The number of stages for this column was set at 20, the optimal feed stage was stage 15. The reflux ratio was set to 5, while the boilup ratio was kept at 2. This boilup ratio allowed for a high enough ethanol fraction for column 3, while keeping the ethanol fraction in the bottoms low, as can be seen in the sensitivity analysis in **Figure 14**. This resulted in an ethanol concentration of 92 wt% in the distillate, with no significant loss of product in the bottoms of the column.

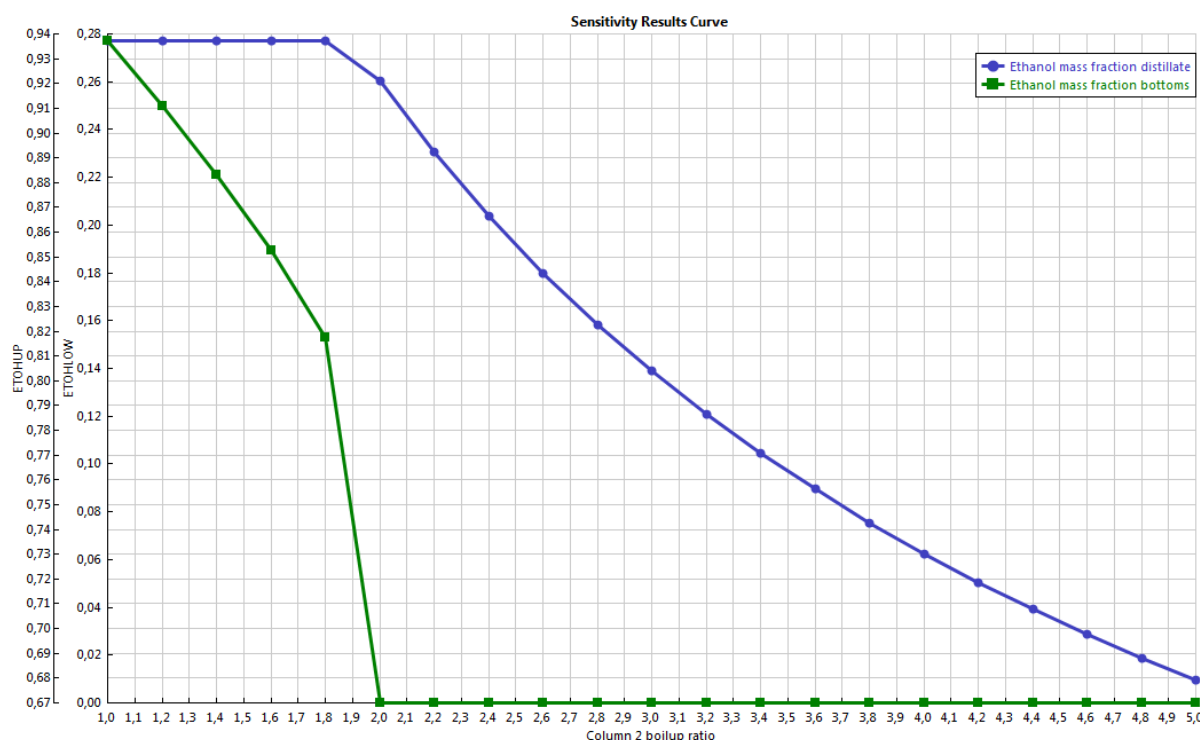


Figure 14: Column 2 boilup ratio sensitivity analysis

Column 3 (4.C-3)

The third column is the actual extractive distillation column. At first this column was modelled with an equilibrium based calculation type. After the first versions of the process were functional, column 3 was modeled using rate-based calculation type. This way of modeling requires additional input parameters for the tray rating: the column diameter, the tray type and the tray spacing. The advantage of rate-based modelling in aspen is that less sizing is necessary; the diameter of the column and the actual number of can be obtained directly from the model. Another effect of rate-based modelling is that Aspen calculates the pressure drop over the column. To accommodate for that, a pump was added before the column, to make sure the feed pressure was higher compared to the column pressure. The column was modelled with sieve plates with a spacing of 0.6 meter. For this column the optimal reflux ratio was found by setting the distillate rate parameter in the RadFrac block, which returns the optimal reflux ratio. The final design was a column with a diameter of 3 meters, 40 plates and a reflux and boilup ratio of 3 and 2 respectively. The boilup ratio was found with the help of the sensitivity analysis in **Figure 15**. The boilup ratio of 2 yielded a very high purity of ethanol in the distillate, while keeping the product loss in the bottoms and the energy consumption relatively low. The solvent was fed to the column at stage 6 and the mixture was fed at stage 32. As in column 1, in this

column 0.1% of the distillate was vented from the reflux drum, to accommodate for the non-condensable gases. One additional parameter is required for extractive distillation: the solvent feed rate. This is usually defined using the solvent to feed ratio, or S/F ratio. The goal was to find a S/F ratio that allowed good separation, but did not need excessive amounts of solvent. The optimal ratio was found to be approximately 1, with a feed flow of 98 ton/h and solvent flow of 100 ton/h. This optimal flow rate was found through a sensitivity analysis, shown in **Figure 16**. The purity of the product increases with the flow of ethylene glycol, however increasing the flow rate past 100 ton/h doesn't yield higher purity anymore.

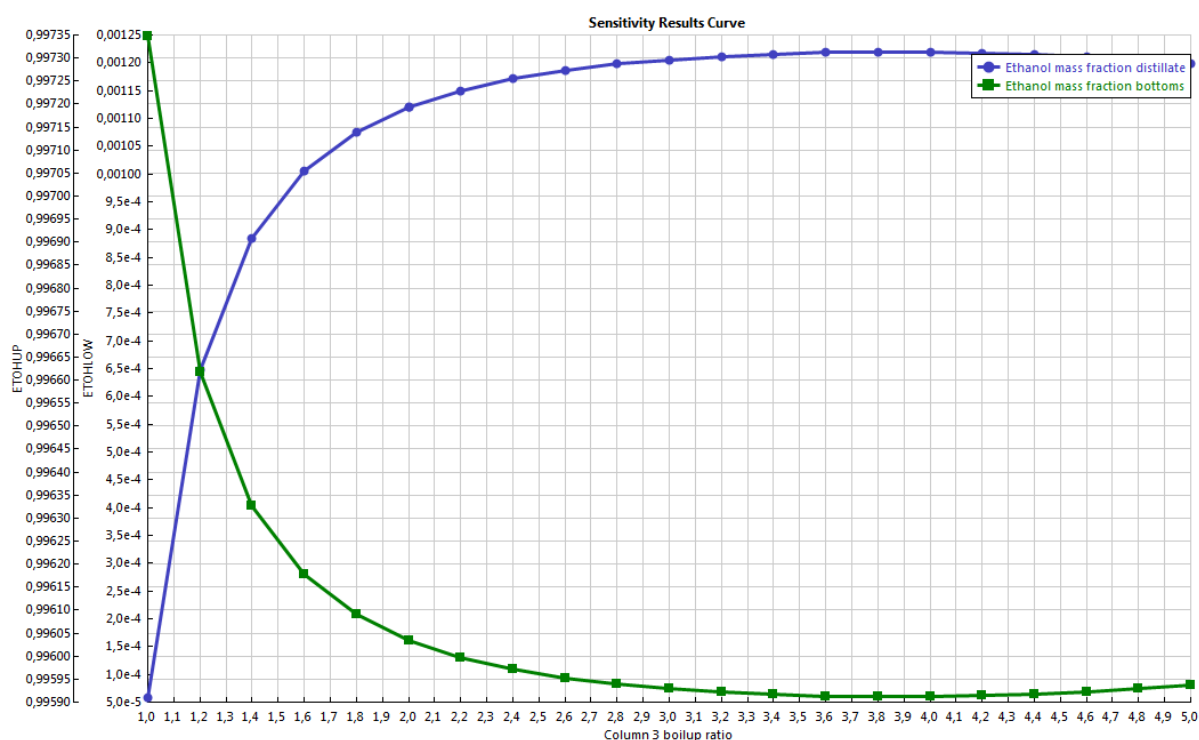


Figure 15: Column 3 boilup ratio sensitivity analysis

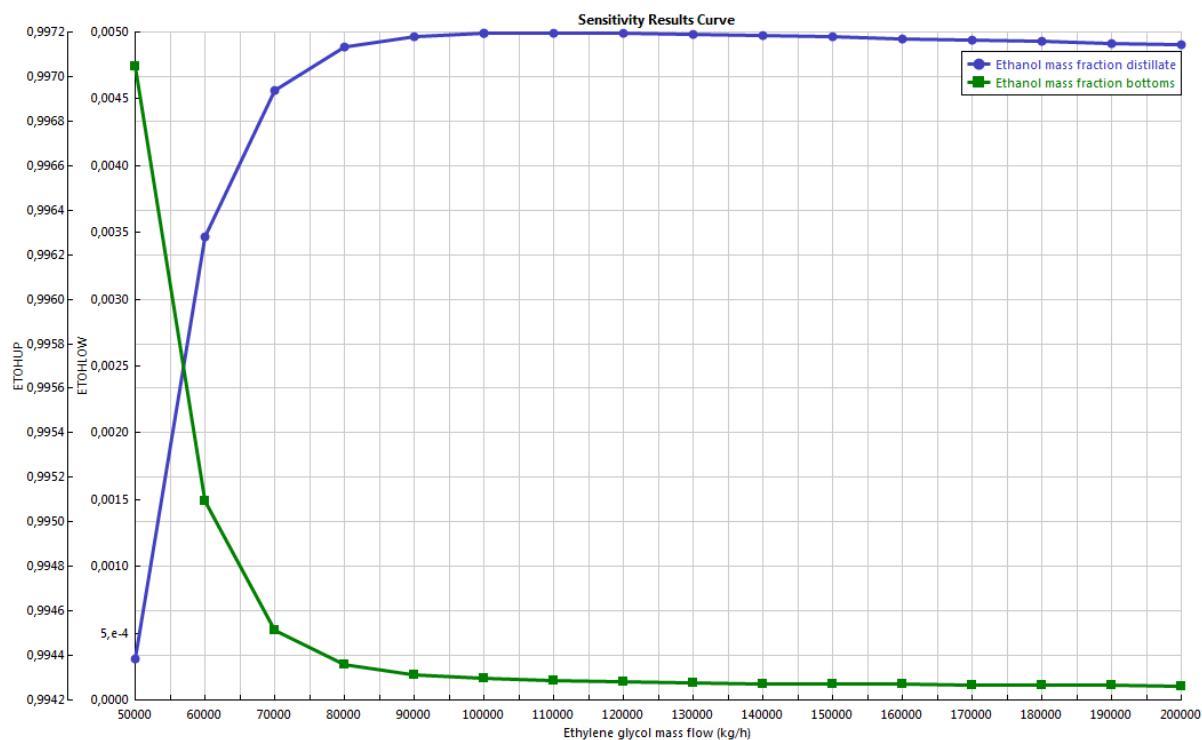


Figure 16: Ethylene glycol feed sensitivity analysis

Column 4 (4.C-4)

The solvent recovery column was once again modelled as an equilibrium based RadFrac column. As mentioned in the introduction, the solvent should be relatively simple to recover. This shows in the optimal column parameters found from Aspen, which are low compared to column 2 and 3. The number of stages was 15, with the feed coming in at stage 11. The reflux rate and boilup rate were 2.15 and 0.6 respectively. The boilup rate was found through the sensitivity analysis shown in **Figure 17**. At this boilup rate the ethylene glycol recovered is as pure as possible. This column recovered 99.95% of the ethylene glycol.

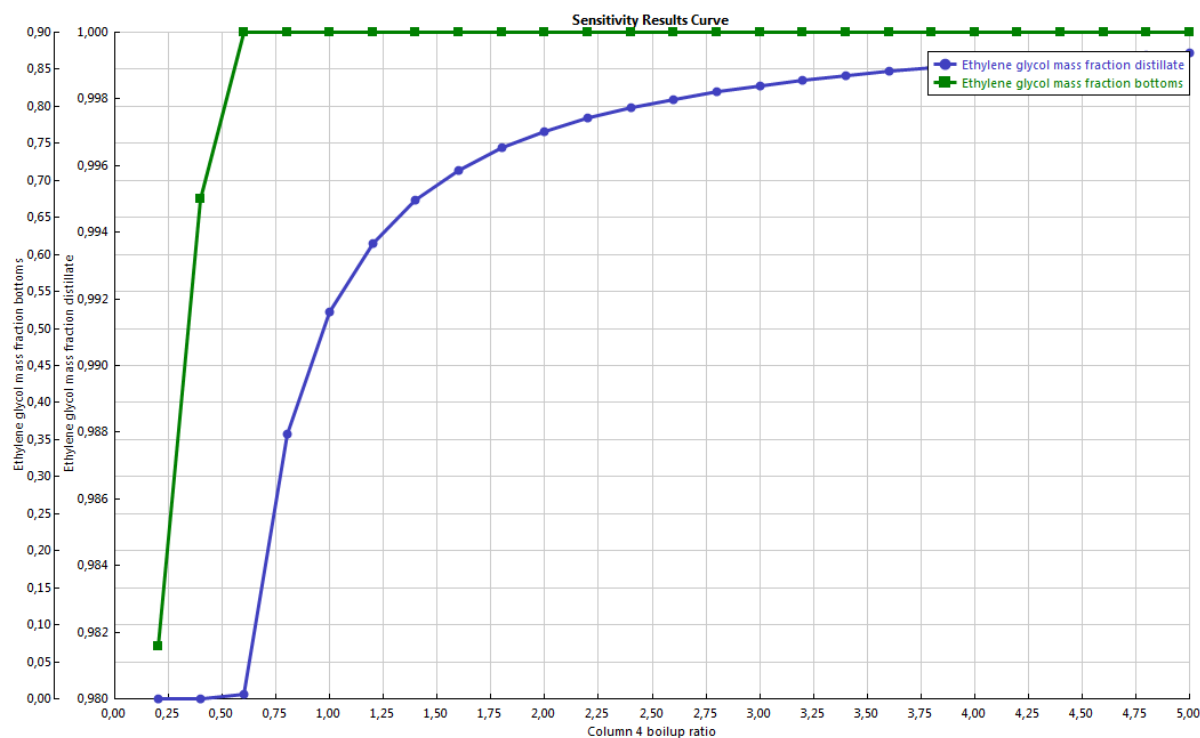


Figure 17: Column 4 boilup ratio sensitivity analysis

Feed pre-heating

To pre-heat the feed, the recovered ethylene glycol from column 4 was used. With this feed, the flow coming from the reactors could be heated from 20 °C to 26 °C. To make the model work correctly, the feed to the first column had to be at 60 °C. To accommodate for this, a second heat exchanger with a duty of 41 MW was required.

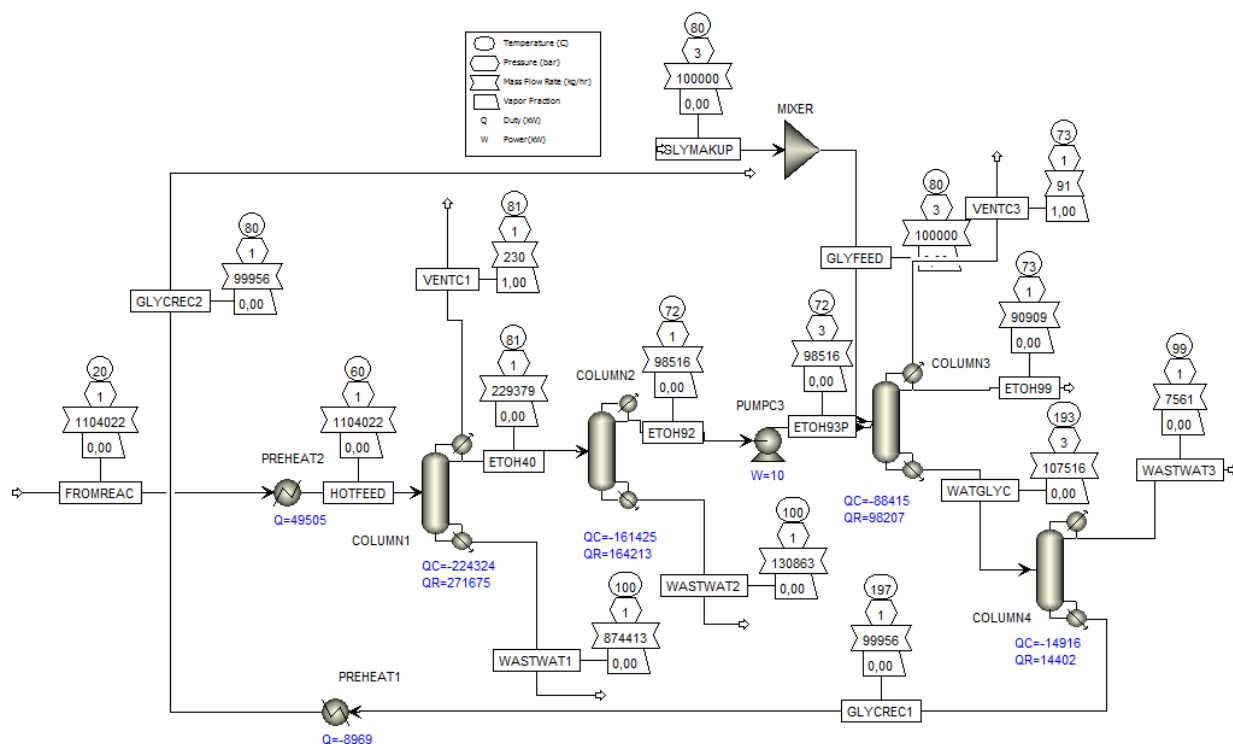


Figure 18: Aspen model makeup section

	Column 1	Column 2	Column 3	Column 4
calculation type	equilibrium	equilibrium	rate-based	equilibrium
number of stages	10	20	40	15
pressure (bar)	1	1	1-3,2	1
reflux ratio	1	5	3	2,15
boilup ratio	0,5	2	2	0,6
feed mass flow (kg/h)	1.104.020	229.374	98.516	107.516
design operating pressure (bar)	1	1	1	1
feed tray	8	15	32	11
solvent mass flow (kg/h)	-	-	100000	-
solvent tray	-	-	6	-
tray type	-	-	sieve	-
plate spacing (m)	-	-	0,6	-
diameter (m)	-	-	3	-

Table 23: Aspen design parameters makeup section

Chapter III - CONTROL AND INSTRUMENTATION

Syngas processing

Figure 19 shows the overall P&ID of the gas processing section, including all auxiliary equipment. The next sections will explain the detailed control, backup and safety systems.

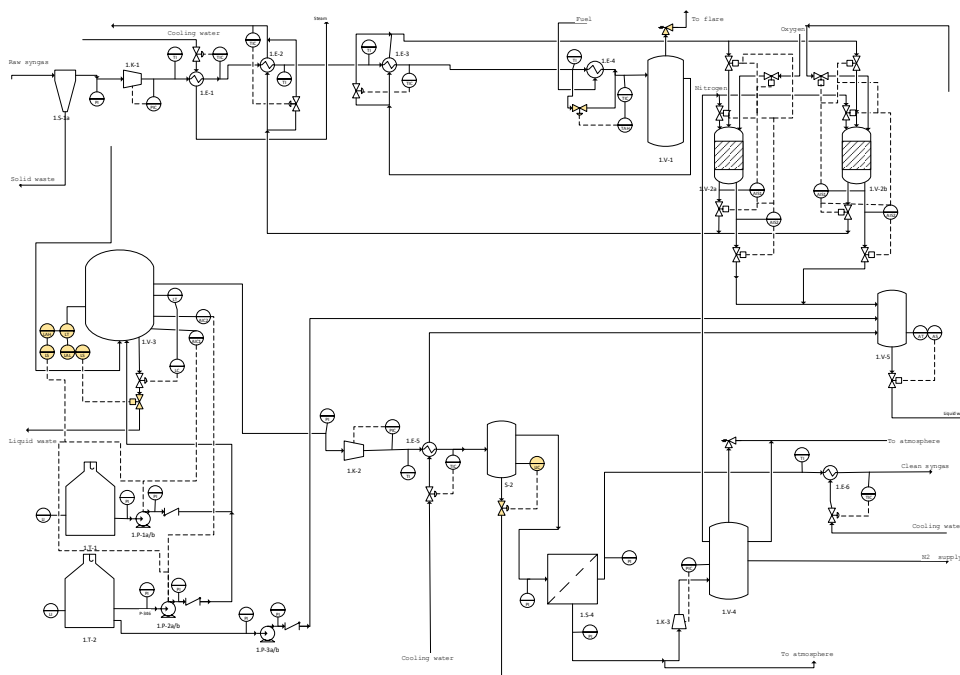


Figure 19: Gas processing overall P&ID. Symbols marked yellow are additions upon HAZOP analysis

Pressure control

As explained in the Process Design section, the gas pressure has to be increased to 10 bar twice. The compressors are responsible for increasing pressure. All compressors have a pressure indicator before compressions to make the pressure known for the operator. The task of each compressor is to increase the pressure to a specific value. If the set value is not reached or exceeded, then a pressure indicator controller detects this difference. What follows is a decrease or increase in the work done by the compressor to reach the set value.

Pressure control is also important for safety. Compression of gas increases temperature. A consequence of a higher temperature is a higher gas volumetric flow rate. When the temperature goes out of control then the heat exchangers are not enough to cool down the gas, endangering the structural integrity of pipelines and equipment.

The pressure is also controlled in the tar reformer vessel for safety. A higher gas inlet temperature will cause a pressure increase in the vessel. The pressure is kept under control by

two systems. The first one is a pressure relief valve. When the gas pressure exceeds a certain limit, gas passes the pressure relief valve until the pressure is stabilized again. The removed gas is brought to a flare where the dangerous compounds are oxidized for safe disposal in the atmosphere. The second step is controlling some gas to bypass the furnace and setting of a temperature high alarm if the temperature is too high. The bypass system will be discussed in the next section.

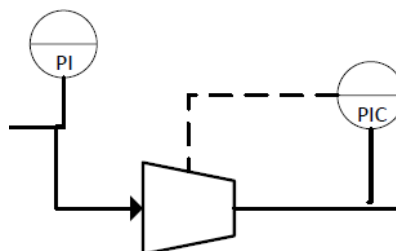


Figure 20: Pressure control

Temperature control

As explained previously the gas processing stage consists of multiple sections operating at different temperatures. To control these different gas temperatures, a couple of heat exchangers and a furnace are designed. The heat exchangers are controlled in two ways.

The first one is when cooling water is used (1.E-1, 1.E-5, 1.E-6). A temperature indicator controller checks if the desired gas outlet temperature is reached. If not, then a temperature indicator controller will control a diaphragm valve to increase or decrease the cooling water flow rate. A higher cooling water flow rate decreases the gas outlet temperature while a lower cooling water flow increases the gas outlet temperature.

The second one is used when no cooling water is used, but two gas stream at different temperatures. The same temperature control system is used for the furnace. It is not possible to control a gas inlet, because the gas streams originate from reactors. If a valve closes, then the gas will be blocked resulting in a higher pressure. When the pressure becomes too high, then the gas cannot be contained. To prevent this and still be able to control temperature, the other heat exchangers have a bypass. A temperature indicator controller controls the bypass flow by increasing or decreasing the diaphragm valve opening. Bypassing more hot gas will increase the temperature of the hot gas while decreasing the bypassing gas flow rate will increase the temperature of the cold gas and vice versa.

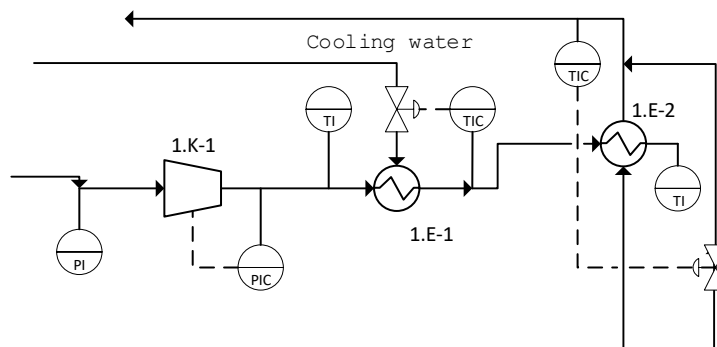


Figure 21: Temperature control

Fixed bed reactor control systems

The three operational stages of the fixed bed reactors are controlled by two analytical indicator switches. AIS1 detects the hydrogen sulfide concentration, while AIS2 detects the oxygen concentration.

The absorption stage will only have the gas inlet and outlet open. As explained previously hydrogen sulfide is absorbed by zinc oxide forming zinc sulfide. After no zinc oxide is left, hydrogen sulfide will come out of the reactor. AIS1 immediately detects the trace amounts of hydrogen sulfide and closes off the gas inlet and outlet while opening the oxygen inlet.

The regeneration stage only has the oxygen inlet open. Oxygen will regenerate zinc sulfide back to zinc oxide. When all zinc oxides are regenerated again, oxygen will come out. AIS2 immediately detects the oxygen and opens the nitrogen inlet and waste outlet.

The flushing stage only has the nitrogen inlet and waste outlet open. Nitrogen flushes all oxygen and sulfur dioxide. When no more oxygen is detected by AIS2, the nitrogen inlet and waste outlet are closed. To go back to the absorption stage, AIS2 also opens the gas inlet and outlet.

When one fixed bed reactor is closed off, i.e. the reactor is in the regeneration and flushing stage, the gas will go to the other fixed bed reactor which is ready for the absorption stage. Therefore no control between reactors is necessary.

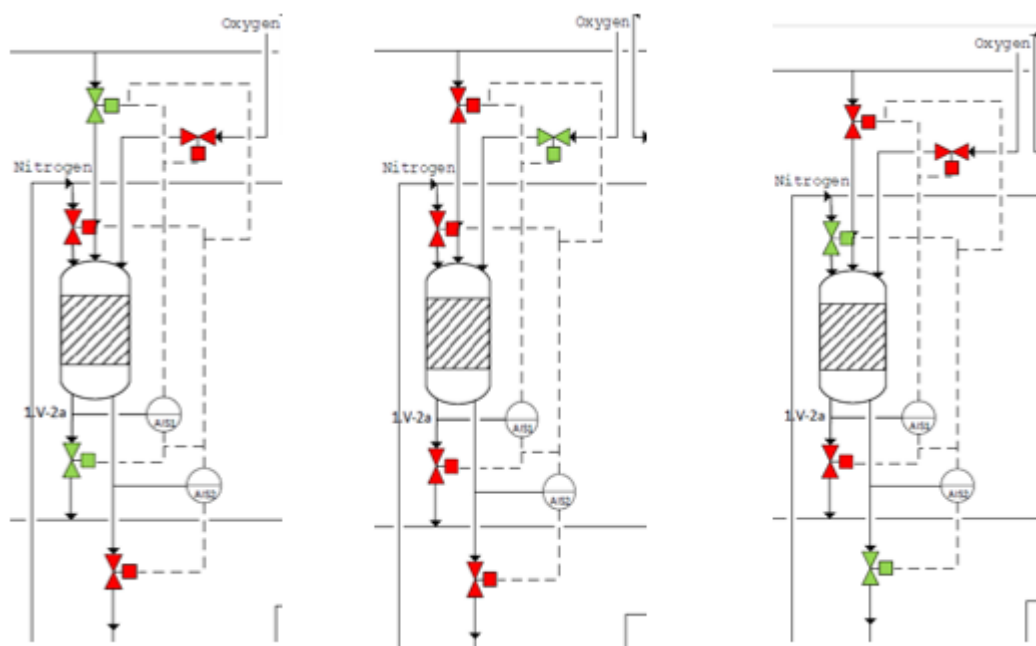


Figure 22: Fixed bed reactor control (green is open, red is closed), from left to right: absorption, regeneration and flushing

pH control

The waste gas from the fixed bed reactor has a high concentration of sulfur dioxide. As explained previously the waste gas is neutralized by sodium hydroxide, water and oxygen. The waste outlet is controlled by an AS. An AT detects the pH levels and transmits it to the controller. When the pH is higher than 5, the vessel content can be safely disposed.

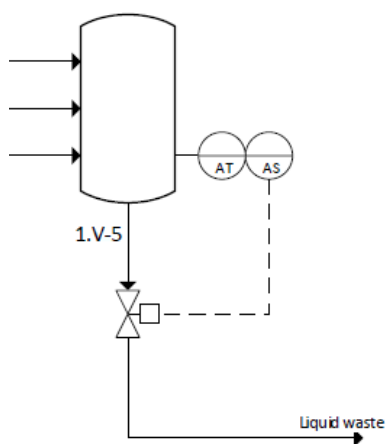


Figure 23: Sulfur dioxide neutralization vessel

Continuous stirred tank reactors

The function of the continuous stirred tank reactor is to absorb nitric oxide and sulfur dioxide in a solution of potassium permanganate and sodium hydroxide. The potassium permanganate and sodium hydroxide varies according to the quantity of nitric oxide and sulfur dioxide in the gas. To decrease or increase the concentrations, two AIC's control the corresponding positive displacement pumps. Asking for less or more fluid pumped whether an increase or decrease in concentration is wanted. The pumps are protected by a check valve in the case of back flowing liquid.

Liquid is removed from the reactor to keep the absorption liquid as pure as possible for an as high as possible conversion. So the reactor needs a way to dispose waste liquid. A level transmitter and level controller operate the liquid level trying to keep the level constant. In an emergency, i.e. when the level is too high or too low. When the level is too high another LT will set off a high alarm and shutting off the pumps to prevent more liquid to come in. When the level is too the same LT will set off a low alarm and closing the liquid outlet.

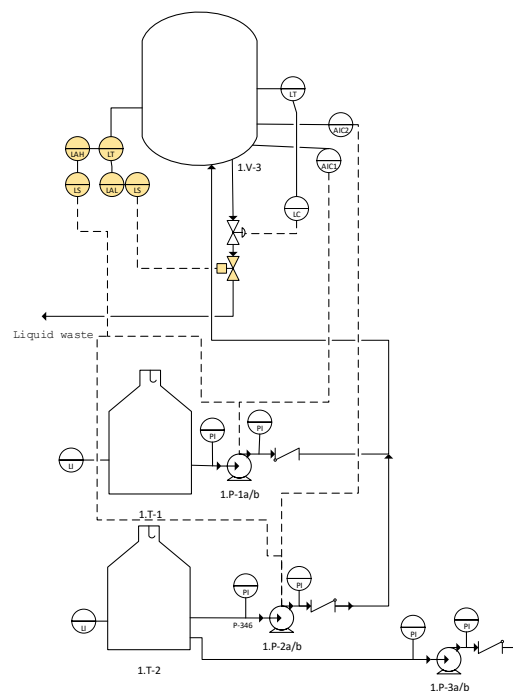


Figure 24: CSTR control and safety system

Shown in **Figure 25** is the full piping and instrumental setup for the growth reactor of the production stage in the syngas to ethanol plant. The reactor as mentioned in the upscale has a liquid volume of 830m^3 and a net volume of 900m^3 . From the bottom of the reactor, a syngas stream is fed that bubbles through the reactor. On the left side of **Figure 25** a number of tanks provide acid, base, antifoam, nutrients, and water to the reactor. Above the reactor, remaining unreacted gasses exit, where they are filtered and passed through two flashers that induce a pressure drop of 9bar then attempt to condense any remaining ethanol or acetate removed as a gas from the reactor. A medium stream is transported from the growth reactor to the product reactor, and a cooling water stream supplies the reactor with cooling fluid for its internal bare coil cooling system. Each section of the P&ID in **Figure 25** will now be examined in closer detail.

As a general note, a single transmitter or indicator shown in the P&ID is considered absolute, and always true, in the sense that in reality there may exist 4 or 5 pressure sensors, but for simplicity, only one sensor per type is shown in the following figures. In the true reactor at least 3 of each type of sensor would be required.

Acid – Base Control

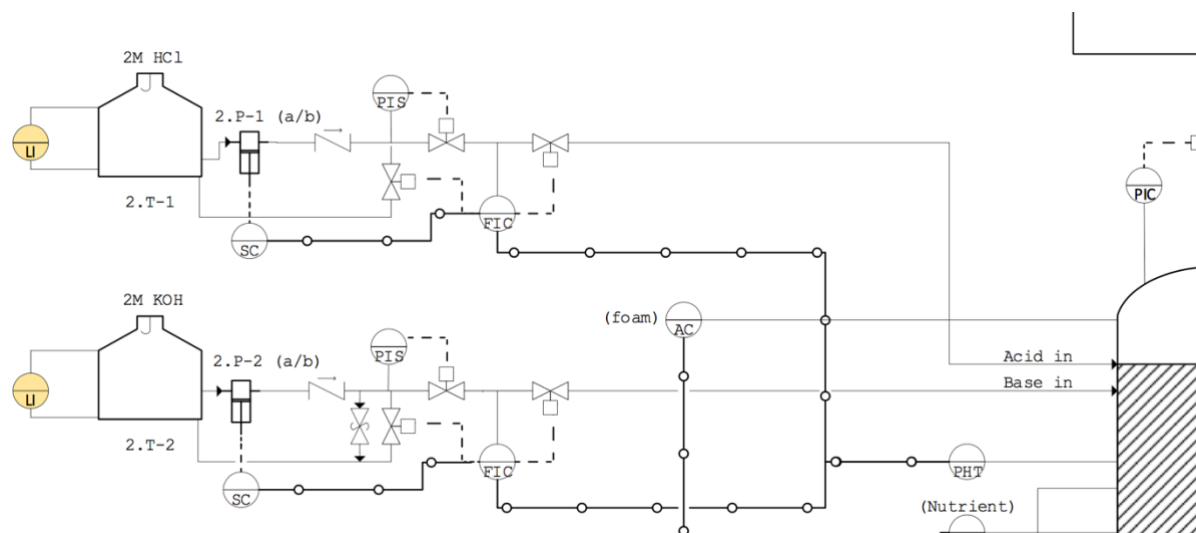


Figure 26: Acid - Base supply - P&ID

The acid and base systems are on demand systems that require input from a pH transmitter. The acid or base flow is requested when the pH exceeds or falls below the desired level. Data is sent from the pH transmitter to the flow indicator controller of either the acid or base supply. Upon request, the FIC starts the pump that is controlled by a speed controller. The pump

increases the fluid pressure by 9 bar. This is needed as the pressure of the acid and base reservoirs are atmospheric, and not increasing the pressure to 10 bar would induce backflow from the 10 bar reactor. Once the fluid pressure has reached 10 bar, the PIS opens a valve that allows media to flow towards the reactor. Finally, the FIC can modulate flow to the reactor by feathering two valves to accurately control flow. A speed controller is not desired for flow control here as the acid and base pumps are only made to turn on occasionally for short periods of time, and therefore don't need accurate speed control. Additionally, the pumps do not require constant flow, and feathering a speed controller to increase pressure to 10 bar, and then when the PIS opens the valve to the reactor, accurately control flow, would be very difficult to control accurately with a speed controller. A speed controller is still used to control the speed of the positive displacement pump, and therefore the rate of flow-recycling (using the relief valve) and pressure increase ahead of the pump. As a safety precaution, a relief valve is placed on the high-pressure side of the pump and opens at 10.5 bar to allow for fluid recycling. Lastly, LIs are placed in both acid and base tanks. The acid and base flows do not mix before entering the reactor. Note, the idea of having two valves is that the pump activity doesn't need to be as frequently changed, but rather some liquid can be recycled back to the tanks, whilst some is transported to the reactor, and the throughput of the pump can remain constant. After HAZOP a scenario where inflow supplies run out was considered, and therefore LI were incorporated.

Nutrient and Water Control

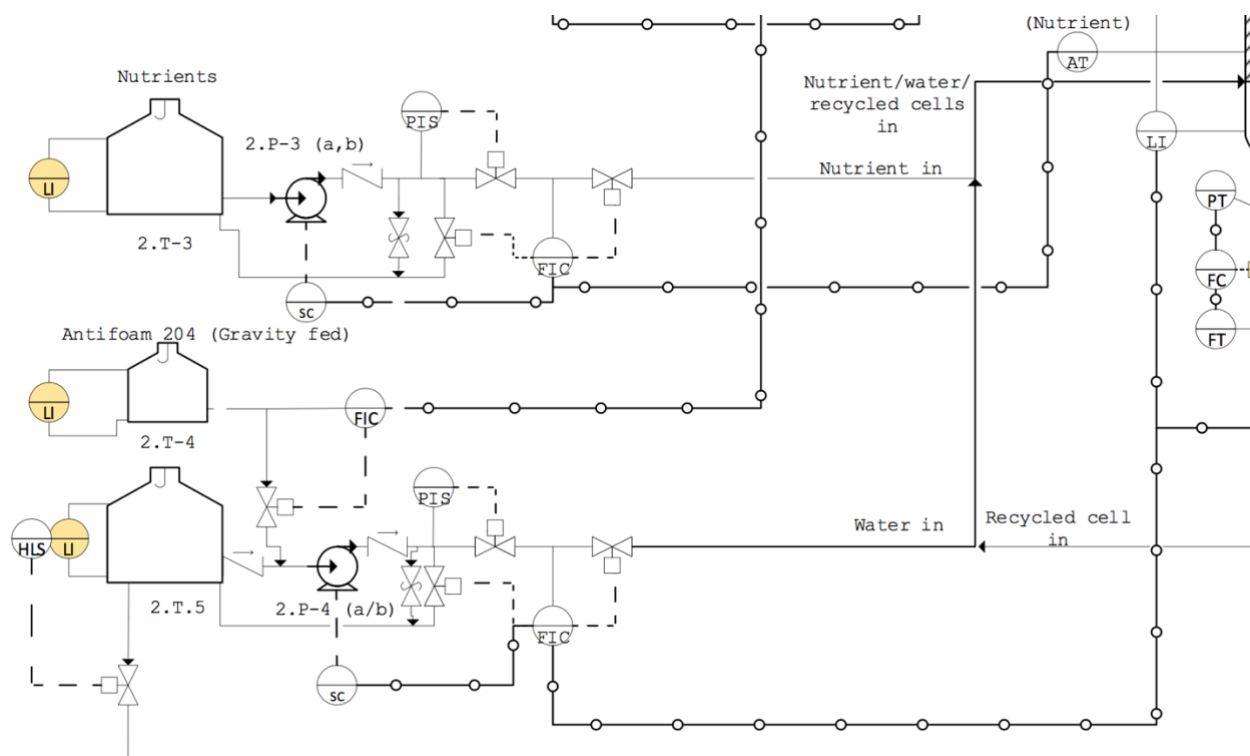


Figure 27: Nutrient, anti-foam, and water supply P&ID

The nutrient, antifoam, and water reservoir are similar to the acid and base tanks as they all are vented, atmospheric tanks with level indicators. The workings of the nutrient tank are identical to the acid and base tanks, but instead operates on a set volumetric flow rate, with additional feedback from an analytical controller which measures the concentration of a particular nutrient in the reactor. The nutrient flow joins the main water inlet prior to entering the reactor. Water and nutrient inflow are a constant flow for this reactor, and therefore a speed controller is used to modulate the flow rate into the reactor. The speed controller is controlled by a FIC which receives information from both a level indicator and analytic controller that monitors EtOH concentration. The level indicator modulates flow by increasing or decreasing it based on the tanks liquid level, and the flow rate can also be increased if more dilution of EtOH is required so not to affect reaction kinetics. Like the other supply tanks, a pressure switch acts as a safety measure to ensure the water inlet is at 10 bar, and as a secondary control measure, valves can be modulated to direct water flow back to the water reservoir, or toward the tank. As a safety precaution, a relief valve is placed on the high-pressure side of the pump to allow for fluid recycling. The water reservoir contains a LI and a High-Level Switch (HLS) to drain water from the reservoir in case the water level gets too high. Antifoam 204 (2.T-4) is a smaller tank

that doesn't have a pump, but upon request from an analytical controller measuring foam levels, will allow flow via a FIC and valve into the main water line. This system is gravity fed and deploys antifoam into the low-pressure end of the water pump inlet (not literally into the suction head but slightly downstream). Antifoam is toxic to the microbes, and a small amount is already present in the nutrient feed to prevent foaming. For these reasons, this antifoam tank will be small and preferably unused, but exists as a safety measure. A cell recycle stream meets the main water line, which mixes with the nutrient stream before entering the reactor via a single inlet. After HAZOP a scenario where inflow supplies run out was considered, and therefore LI were incorporated.

Syngas Out and Product Recovery Control

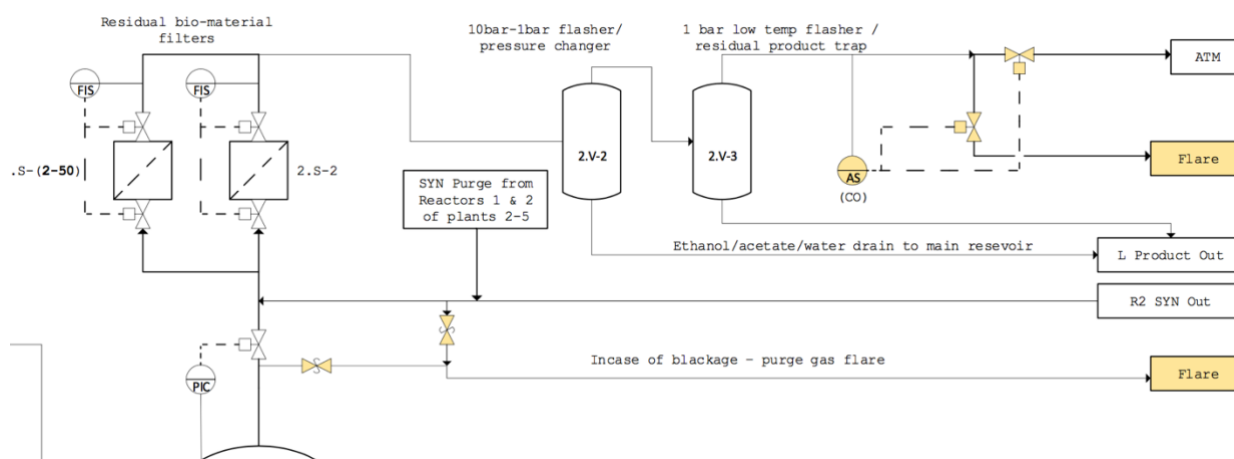


Figure 28: Syngas cleanup and product recovery - Growth Reactor - P&ID

Figure 28 displays the syngas cleanup and product recovery stage. The incoming stream seen at the bottom of **Figure 28** is connected to the top of the growth reactor. Because the pressure of the reactor must be well modulated to prevent large variations in pressure that could damage the microbes, a PIC is attached to a valve to modulate reactor pressure. Due to the stoichiometric amounts of gas used, a limited flow of unreacted gasses is found at the outlet, and the flow of the growth reactor is combined with the gas outlet of the product reactor (R2 SYN OUT). Additionally, the gas out-flows of all five parallel plants are combined here to clean the gas in a single flow scheme. Primarily, the combined syngas is passed through 1 of 50 modular high flow membrane filters that filter out organic matter or microbes carried in the gas outflow. A FIS monitors the health of each filter, and in case of low or no flow, the switch is activated, stopping flow through the filter and indicating that the filter must be replaced. The gas then passes through a flasher that reduces the pressure to 1 bar, and a secondary flasher that

cools the gas to condense any ethanol and acetate left in the gas feed. Both 1 bar liquid streams are then transported to a product reservoir (L Product Out) discussed in the stage 2 P&ID. The final gas outlet passes by an analytical switch (AS) that measures CO concentrations. According to the Guidelines for Air Emission Regulation, CO emissions from installations should not exceed 83ppm or 100mg per m³ ³⁹. The AS therefore checks what the CO concentration is and switches the flow between a flare and open atmosphere. This is desirable as the outlet gasses mostly consist of N₂, and it would be uneconomical to try to heat and burn large flows of N₂ and to get rid of trace amounts of CO. Lastly, in case of flow blockage in the filtration system, a relief valve directs flow to a flare, and in case of back up at the PIC valve in the reactor, a separate relief also directs flow to a flare. After a HAZOP, it was found more care should be attributed to the disposal of CO, and the flare system was incorporated.

Liquid Out and Cooling Control

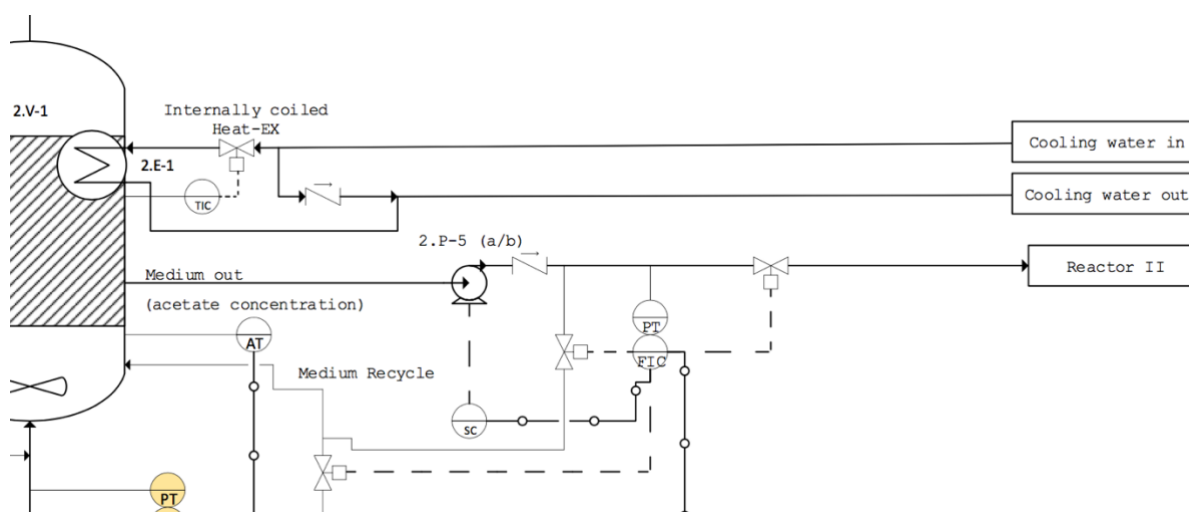


Figure 29: Liquid out and cooling control for growth reactor – PID

The final auxiliary control systems surrounding the reactor itself are the liquid outlet stream, and cooling stream system. To maintain a cool reactor, and limit agitation of cells by pumping media through an external heat exchanger and back into the reactor, a cooling stream of 18°C water is passed through an internal bare cooling coil. Flow is expected to be constant, and therefore a system exists for only slight modulation of heat transport away from the reactor. This exists in the form of a TIC that controls an inlet water flow to the coil by altering the amount of cooling media accessing the internal cooling coil. Cooling liquid that is not able to pass through the coil due to the constriction of the flow may bypass the system using a check valve. This valve would need to be spring loaded or calibrated to not open unless flow is being

restricted to the main cooling coil. This would most likely be opened at a certain pressure (via the check valve itself without any external control). The media out is a steady flow in this system, and the pump again employs a speed controller to modulate flow rate. This speed controller receives input from a FIC, that receives input from a pressure transmitter, analytical controller, and level indicator. Much like the water inflow, liquid outflow must be modulated to control things like the level of liquid in reactor 1 and the steady state concentration of EtOH or acetate in the reactor. The FIC not only controls a SC for the pump, but also a system of valves to help control flow. Primarily, a media recycle valve system exists that redirects flow back into reactor 1 if flow to reactor 2 is in excess. Finally, a purge line exists for when liquid must be removed from the reactor but cannot pass to stage 2. When purged, it can be transported to a safe location (TSL).

Reactor Control

Almost all control systems have now been referenced in the previous control systems discussed, but a final overview of the controls surrounding the growth reactor (2.V-1) is shown in **Figure 30**. Undiscussed features that pertain to the reactor and discovered during a HAZOP was the need to include measures to maintain the reactor under shutdown/unreliable syngas feed parameters. Therefore, a PT and FIS (Flow Indicator Switch) was added to the inlet syngas stream of the reactor. This is the vertical stream directly beneath the bottom of the reactor in **Figure 30**. When low pressure or flow is detected, the switch closes a valve, and syngas inflow is stopped. Next, a second inlet may be opened to maintain a 10bar atmosphere in the tank. This is an inlet feed the also enters beneath the reactor by joining the syngas piping above the syngas safety switch. This safety line is connected to a 20bar N₂ storage vessel, and flow is controlled by a FC and valve which receives data indirectly from a FT and PT. The FT allows the system to acknowledge there is a problem with the syngas

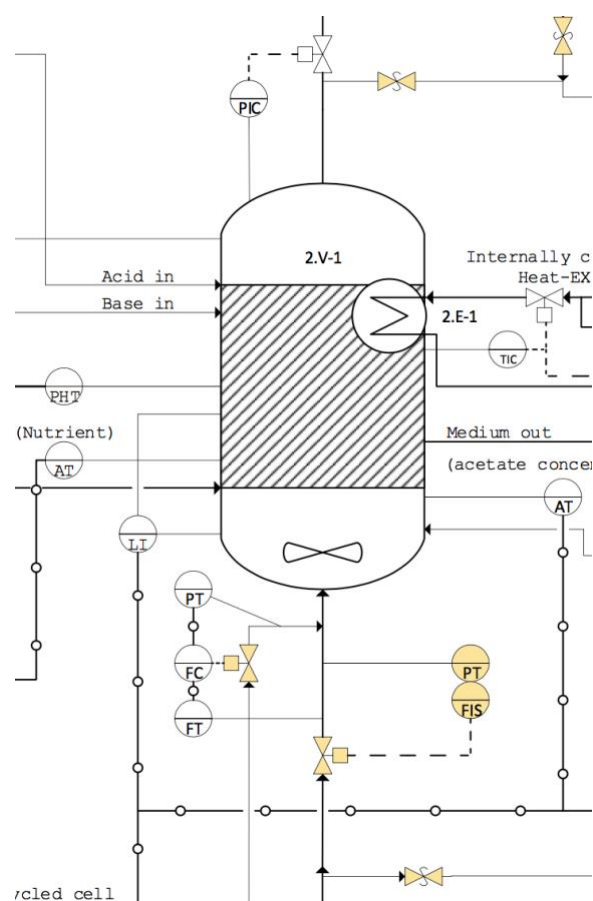


Figure 30: Reactor Control - Growth reactor – PID

problem with the syngas

In **Figure 31**, the overall P&ID for the second stage along with all auxiliary equipment that follows can be seen. Throughout the next sections, each of the control, backup, and safety systems for the majority of process critical equipment will be detailed on.

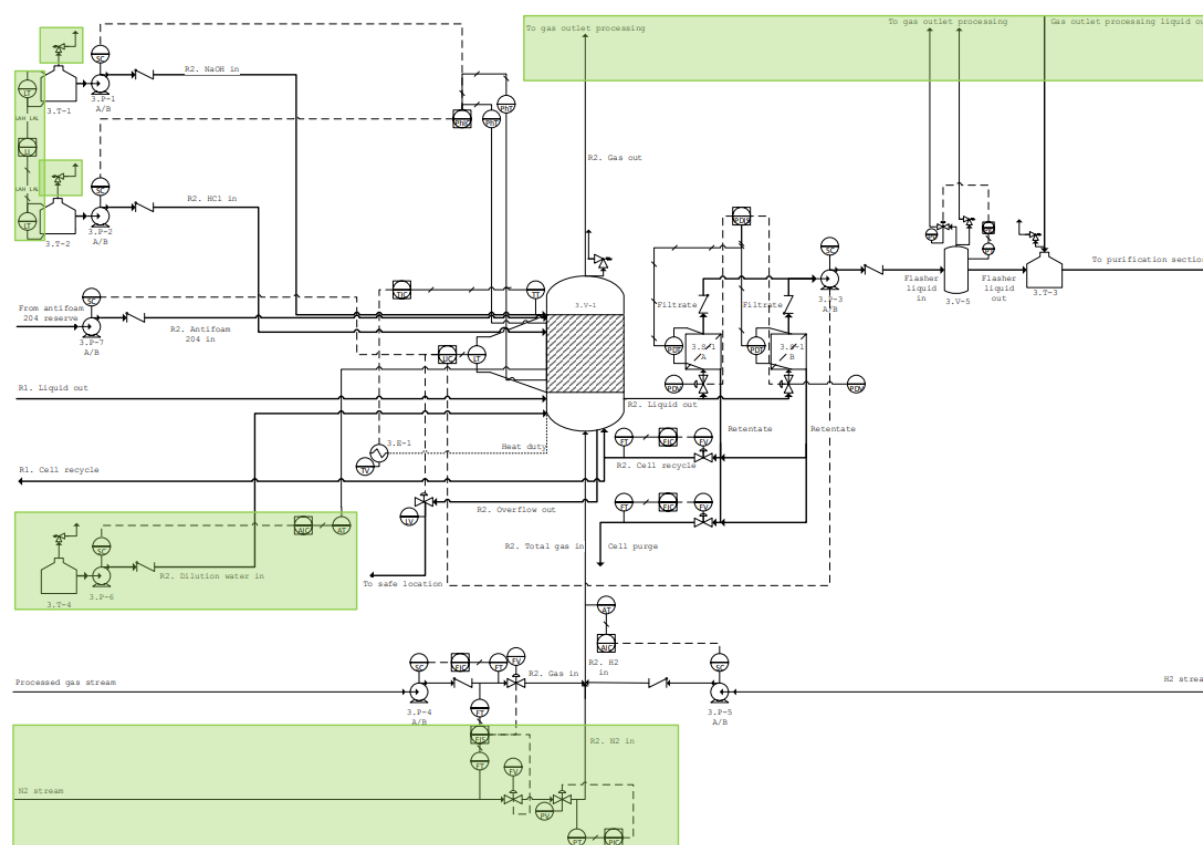


Figure 31. R2 overall P&ID. Marked with green shaded zones are addition upon HAZOP analysis. An enhanced version for readability can be found in the production reactor section in appendix 3.

pH control system

As previously explained, reactor pH is among one of the most important operating parameters for the bioreactor as it governs the direction at which the equilibrium in the WLP proceeds, and therefore what metabolites were produced in which stage. As R2 is a solventogenesis type of reactor which produces primarily ethanol, the optimum pH to achieve the desired outcome is between 4.4-4.8, slightly more acidic relative to that of R1. This operating pH can be seen as a method of tipping the equilibrium between acetate and ethanol, as maintaining low pH would promote the conversion of acetate into ethanol, as a way for the microbe to try and increase the pH by reducing the amount of acetic acid present in the liquid (Le Chatelier's principle).

The control of reactor pH in the case of R2 can be seen in **Figure 32**. The design reported in this thesis proposes the use of two reservoirs, namely 3.T-1 and 3.T-2, containing a solution of NaOH 2M and HCl 2M, respectively. Each of the acid and base reservoirs were also equipped with a level transmitter (LT), connected to a level indicator (LI) with a level alarm high (LAH) and low (LAL) as a precautionary measure to notify an operator if either of the reservoirs were about to be empty, which will then be followed by a manual refilling of the said reservoir. This, however, was not expected to occur with high frequency as, in addition to the relatively low volumetric requirement of the acids and base solution by the process, the reservoirs are also specified with a volume large enough to handle the pH requirement of R2. As a safety measure, each of the reservoirs, while operating at an atmospheric pressure of 1 bar, were equipped with a relief valve to prevent over-pressurization, leading to possibly stress cracking and loss of containment.

The decision making pertaining to which solution should be added to the reactor and also the quantity required to achieve the desired operating pH were handled by a pH indicating controller (pHIC), receiving information from two pH transmitters (pHT) in the reactor, controlling two speed controlled (SC) dosing pump on two separate lines, for acid and base each, along with a check valve on each line to prevent backflow of reactor materials into the acid and base reservoirs. The use of two pHTs were considered sufficient based on the fact that R2 is a microbubble sparged bubble column, which due to the very well-defined bubble circulation throughout the column behaves very much like a CISTR, thus implying that quantities such as temperature, concentration, and pH, can be considered to be uniformly distributed throughout the entire reactor.

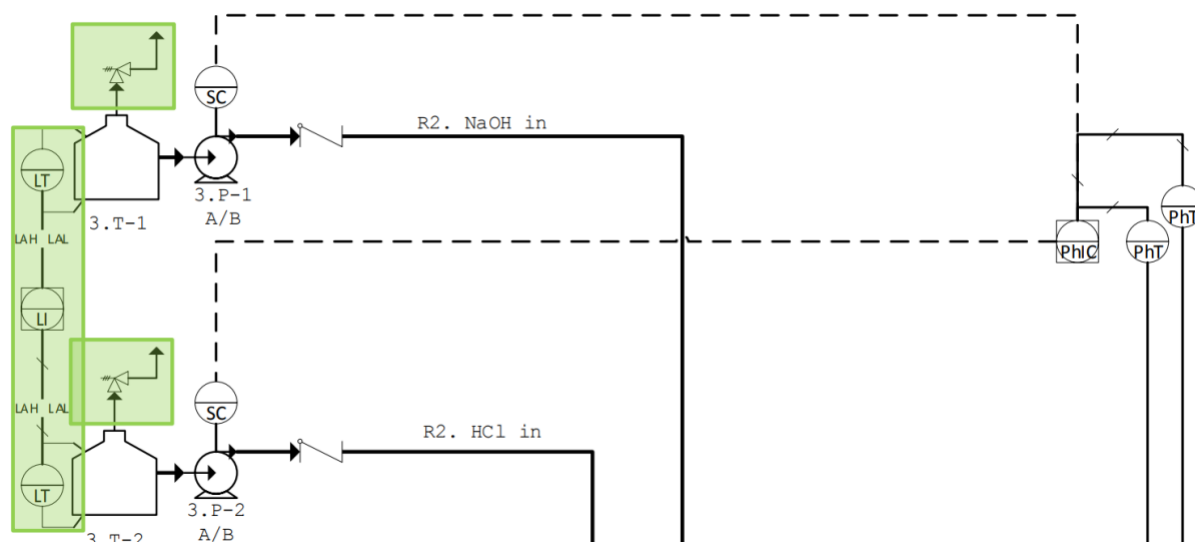


Figure 32. R2 pH control system

Foaming control system

Due to the relatively high cell density in R2 and the large gas inflow stream, foam formation in the reactor becomes an important issue to address, as excessive foaming can lead to the blocking of some of the streams and trapping of gases, which might lead to catastrophic events of over-pressurization, overflowing reactor, and loss of containment.

The reported design, as shown in **Figure 33**, proposes that foaming event in the case of R2 can be controlled by controlled addition of antifoam agent Antifoam 204 into the reactor when necessary. The control system proposed omits the inclusion of a container for the said antifoaming agent, considering the relatively small amount required by the process, estimated to be averaging at 2.6 m³/h of antifoam 204 volumetric flowrate, scaled up linearly with the reactor volume and dilution rate from a value of 0.24 mL/h, as reported by the pilot-scale experiment.

The decision-making pertaining to when the solution of antifoam 204 should be added to the reactor and also the quantity required to lower the foaming level were handled by a LIC, receiving information from a LT in the reactor, which in this case is a dual-purpose LT, transmitting both liquid and foam level simultaneously to the LIC. Similar to that of the pH control system, the LIC controls an SC dosing pump on the line for the antifoaming agent, equipped also with a check valve to prevent backflow of reactor materials.

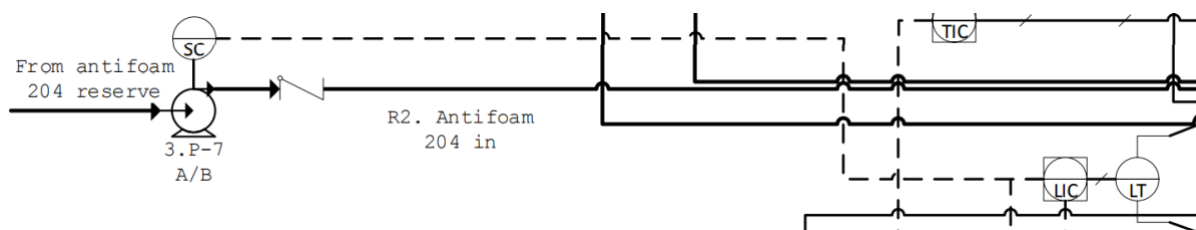


Figure 33. R2 foaming control system

Primary metabolite steady-state concentration control system

While the dilution rate in the proposed design has been scaled up to accommodate for the enhanced productivity, such that the steady state concentration anywhere in the reactor never surpasses a threshold point of diminished kinetic, in the event of issues pertaining to the other sections of the process, or simply to fluctuations of production rate, an auxiliary dilution system is of importance.

The reported design shown in **Figure 34**, proposes the addition of a water reservoir, 3.T-4, as a backup system to supply additional water into R2 if additional dilution is required. The decision-making pertaining to when additional water inflow is needed by the reactor and also the quantity required to lower the steady state concentration within the reactor, down to a safe target value was handled by an analytical indicating controller (AIC), receiving information from an analytical transmitter (AT) in the reactor, which in the case of R2 is measuring the concentration of ethanol, being the primary metabolite in a solventogenesis reactor. Again, similar to that of the foaming control system, the AIC controls an SC dosing pump on the line for the water stream, equipped also with a check valve to prevent backflow of reactor materials. Finally, as a safety measure, the water reservoir, while operating at an atmospheric pressure of 1 bar, was also equipped with a relief valve to prevent over-pressurization.

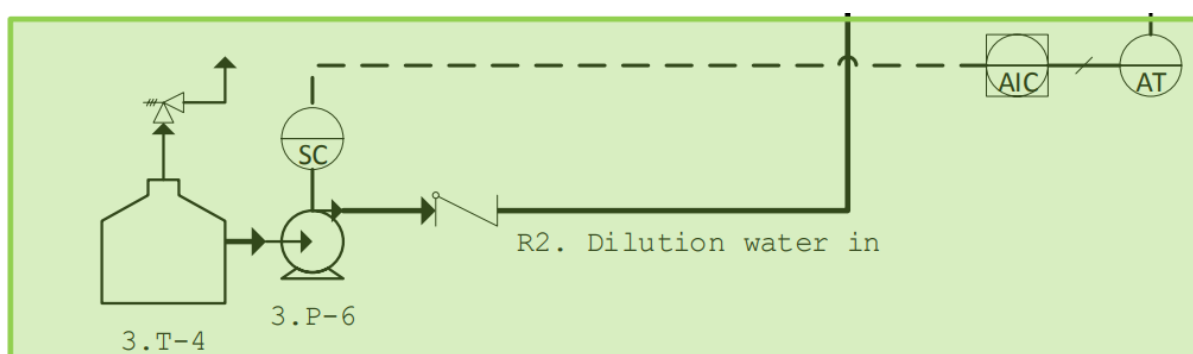


Figure 34. R2 primary metabolite steady-state concentration control system

Gas inlet control system and pressure loss safety measures

As the reactors were scaled up based on a specific production capacity, it is, therefore, important to control the inflow of gas into the reactor. Furthermore, since the reactors operate at 10 bar of pressure, controlling gas inflow into the reactor also act as a mean of maintaining reactor pressure. While it will be further elaborated in later sections, it is worth noting that the pump symbol, in any instance of gaseous component transportations refers to a gas blower/fan equipment, thus implying that the pump symbol was used universally to represent a transport equipment.

The reported design shown in **Figure 35**, proposes a mean of controlling the reaction gas inflow and also adding a switch mechanism as a failsafe measure in an event of failure, either in other sections of the plant, or the reactor itself, which might cause a case of pressure loss in the reactor. The control and safety system showed consists of primarily a flow indicating switch (FIS), which receives flow transmission from two FTs, measuring the flow of gas in two separate lines of gas inflow, one being an N₂ line, and the other being a reaction gas (syngas) line. The switch primarily depends on the flow being measured in the reaction gas line, which, in the event of imminent pressure loss, such as, for example, due to a cut-off in the reaction gas stream. The FIS will then set to trigger the opening of the valve in the N₂ line to then compensate for the loss of reaction gas stream. Also, similar to that of the previous flow related control systems, another FT is also present on each of the lines, N₂ and reaction gas, reporting to their corresponding FIC, controlling an SC pump to then modulate the flow rate depending on the specific need at any point in time.

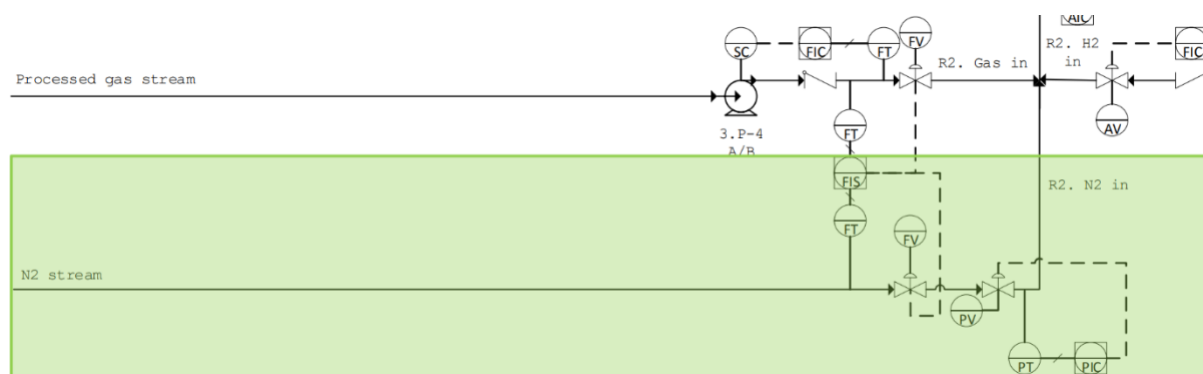


Figure 35. R2 gas inlet control system and pressure loss safety measures

Gas inlet composition control system

As can be seen in **Table 8**, the two reactors, R1 and R2, each has different mol fraction of H_2 in their gas feed, which is 0.38 for R1, and 0.55 for R2. This, therefore, implies the need of an additional H_2 inlet stream to compensate for the extra H_2 need in the gas inflow to R2 if the composition of the processed reaction gas is assumed to match that of R1's need.

To solve the aforementioned issue, the design presented in this thesis, shown in **Figure 36**, proposes a method of controlling the reaction gas inflow composition. The control system is shown to consist of primarily an AIC, receiving a transmission on the concentration of H_2 in the flow from the AT located directly on the line of gas entering R2. The AIC will then decide how much additional H_2 is required and will control an SC dosing fan, e.g. a pulse-width-modulated (PWM) fan, to supply the required H_2 to get to the desired gas inlet composition for R2. Additionally, the control system proposed omits the inclusion of a container for H_2 , by assuming that the H_2 can be sourced from either a commercial source or somewhere else within the overall process.

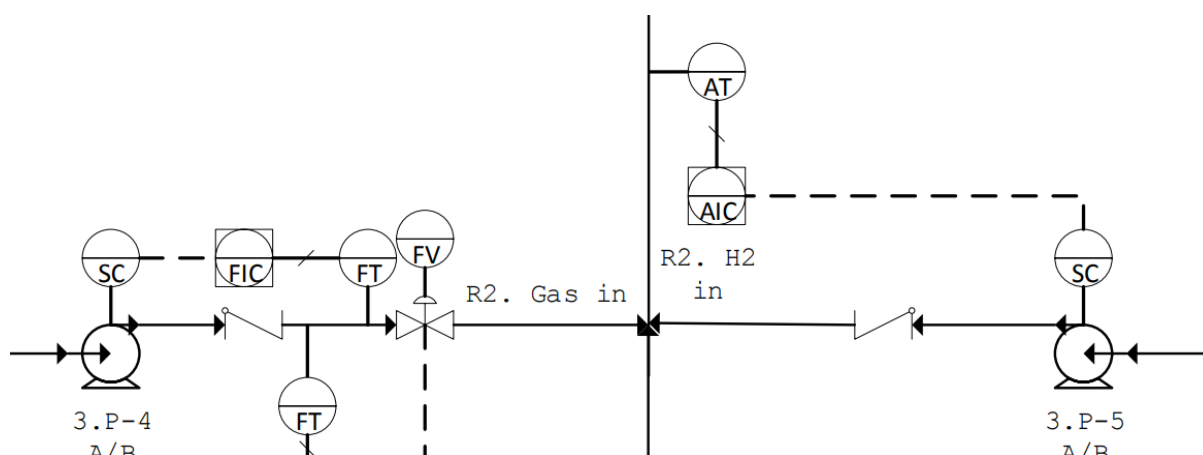


Figure 36. R2 gas inlet composition control system

Reactor pressure control system and safety measures.

As discussed in prior sections, both of the reactors operate at an elevated pressure of 10 bar. Therefore, it is important for this pressure to be maintained, preventing and providing countermeasures against pressure loss or over pressurization, such that it will not lead to catastrophic process failures and loss of containment.

To achieve the aforementioned control, the design shown in **Figure 37**, proposes a method of controlling while simultaneously acting as a safety measure for reactor pressure. The

aforementioned control and safety measure regarding pressure, much like the previously described vessels, was achieved using a relief valve to prevent over-pressurization, specified at over 10 bar relief spring.

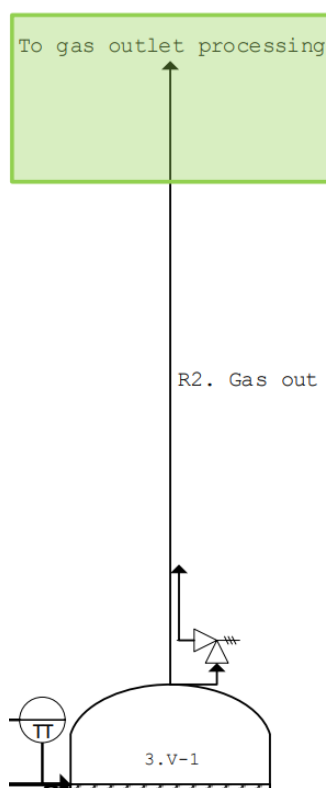


Figure 37. R2 reactor pressure control system and safety measures

Reactor temperature control system

Much like reactor pH, the reactor temperature is also one of the most important operating parameters for bioreactors, since microbes tend to be very sensitive to temperature changes. Upon deviation from the operating temperature of 35°C, productivity ratio can be affected significantly, and in more devastating cases, deactivation of the biocatalyst can occur, resulting in potentially a shutdown of the continuous process.

The control of reactor temperature in the case of R2 can be seen in **Figure 38**, indicated by rectangles of red outlines. The design shown here consists of a temperature indicating controller (TIC), receiving a transmission from a temperature transmitter (TT) in the reactor, which then controls a cooling element, specified as an internal reactor coil, to cool the reactor until it reaches the target steady state operating temperature of 35°C. For the same reason stated in the reactor pH control system, the use of one TT can be considered sufficient due to the uniform temperature distribution.

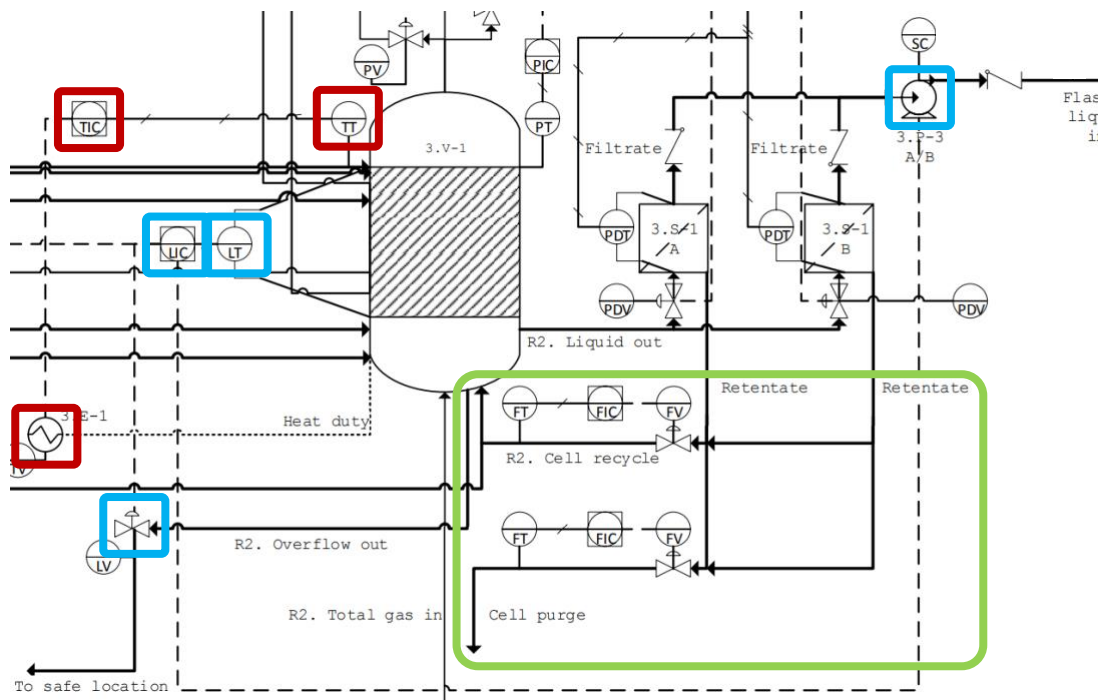


Figure 38. R2 reactor temperature (red), liquid level (blue), and cell recycle (green) control system

Reactor liquid level control system

Much like the foaming control system, reactor liquid overflow which might lead to catastrophic events of over-pressurization and loss of containment. It is, therefore, crucial to add a system to control the liquid level, maintaining it within the reactor tolerance level.

The reported design, as shown in **Figure 38**, marked in blue rectangles, proposes to control reactor liquid level in two ways. One is by having an overflow drain valve at the lowest point of the reactor to drain the liquid overflow to a safe location, which opening and closing of the valve to be modulated by the LIC, depending on the liquid level in the reactor, measured by the LT, the same transmitter mentioned earlier in foaming control system. A second measure of controlling the liquid level in the reactor can be seen to be done by modulating the liquid outflow, which is achieved by controlling the SC liquid outflow pump, to either increase or decrease the flow rate depending on the need to control reactor liquid level.

The described control design was proposed mainly due to its advantage of being relatively independent of any other sections of the plant, thus implying that any sections of the plant can, in principle, operate independently with respect to each other while still having some amount of error tolerance. The proposed design by no means intend to reroute the reactor outflow into

a drain indefinitely and regardless of the extent of the overflow event. It is very probable that in the event of a more catastrophic failure, where the reactor overflow outside the control system tolerance, a system shutdown and diagnostic will be required.

Cell recycle control system

While not much of a control system, the cell recycle system can be seen to be a means in regulating how the cell mass in the retentate stream split three ways between a cell purge stream, a recycle stream to R1, and a recycle stream to R2.

As can be seen in **Figure 38**, marked in green rectangles, the splitting of the cell mass retentate stream leaving the filtration module was achieved using two valves on two separate lines, a cell purge and cell recycle line, controlled by two separate FICs, receiving information of flow from two separate FTs, which will then govern how much the valves open or closes, thus modulating the purge and recycle fraction. From there, the recycle stream will then be physically split two ways between R1 and R2 cell recycle stream.

Cell filtration module control system

Since the filtration modules will be handling a slurry of microbial cells suspended in a liquid medium, it is likely that the modules will get clogged by dead microbial cells after a while and would have to be replaced. Due to the continuous nature of the process, however, the flow would then have to be redirected, such that the entire process would not have to be shut down only to replace a filtration module.

To achieve the described control, the design shown in **Figure 39**, indicated in the green rectangle, proposes the addition of a backup system for the cell filtration module. The design essentially added a second cell filtration module on the parallel arrangement with respect to the other module. Furthermore, the point of clogging and therefore redirection of flow can be determined by measuring pressure drop over the filter module, which is done by the pressure drop transmitters (PDT) on each of the filtration modules. The transmitters will then report to a pressure drop indicating switch (PDIS), which will decide and control if the valve to one of the filtration module would have to be closed to then redirect the flow to the backup module by opening the valve going to the said module, while the clogged filtration module is being either manually replaced or cleaned.

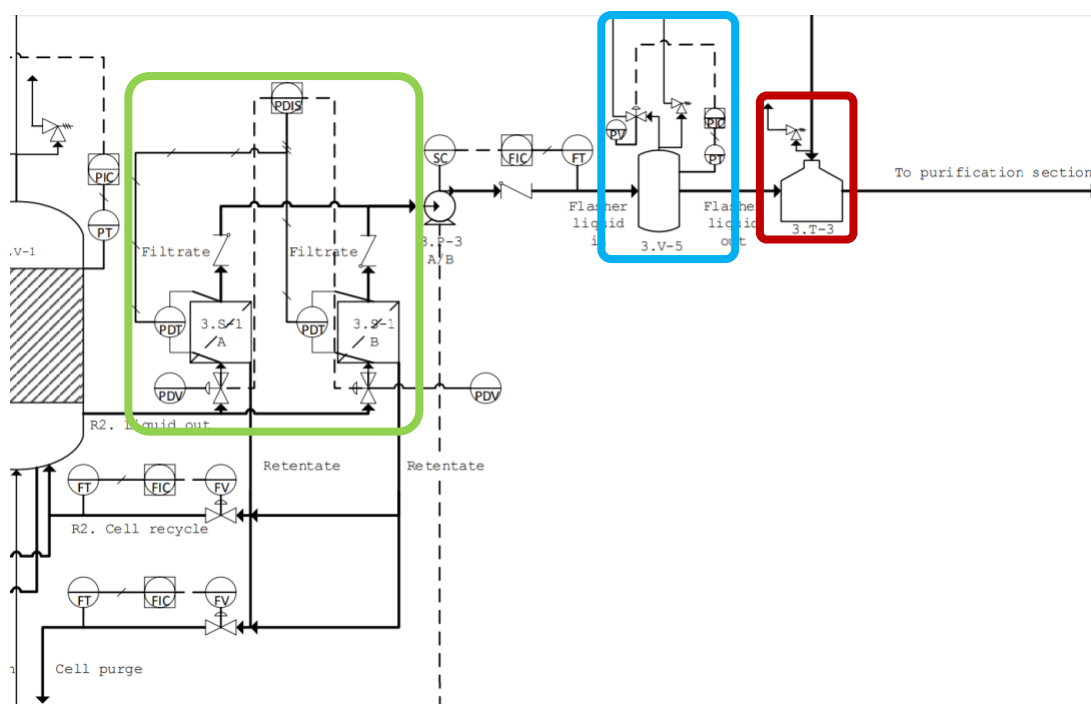


Figure 39. R2 cell filtration module (green), flasher pressure (blue), and liquid storage pressure (red) control system

Flasher pressure and liquid storage pressure control system

As the flasher aims to depressurize the liquid outlet of the reactors from 10 bar to an atmospheric pressure of 1 bar, mainly to reduce the number of dissolved gases in the liquid and to also lower storage cost by eliminating the need of a pressure storage vessel, due to the relatively large pressure drop, it is important for the flasher to be able to vent the gas slowly, to avoid liquid bursts out of the flasher through the venting stream.

To achieve the described control, the design shown in **Figure 39**, marked in blue rectangles, proposes the use of a PIC, receiving vessel pressure information from the PT, which will then modulate the opening of the venting valve to slowly allow the flasher to eventually equilibrate at 1 bar of pressure. Additionally, as a safety measure, much like any of the previously described vessels, a relief valve to prevent over-pressurization, was also added. Similarly for the liquid storage vessel, marked in the red rectangle in **Figure 39**, operating at an atmospheric pressure of 1 bar, a safety measure in the form of a relief valve to prevent over-pressurization, was also added.

Product Work-up

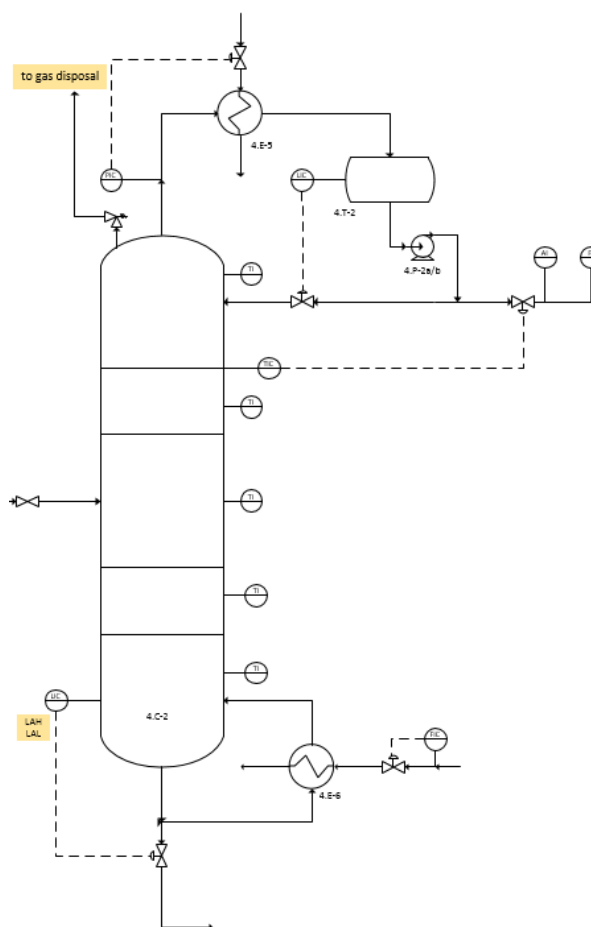


Figure 40: Control system columns 1,2 & 3

To ensure correct working of the system, several control system need to be implemented. The control elements can be found in the P&ID in the appendix. All control systems will be discussed below. According to Towler's book⁴⁰, there are five degrees of freedom in a distillation column that require control. These degrees are the coolant and the steam flow, the bottoms and the distillate rate and the reflux rate. The feed into the columns are controlled by the preceding equipment in the system. The control systems for the first three columns are identical, whereas the control for the fourth column is slightly different. This different is derived from the fact that the desired product from the first three columns is in the distillate, for the fourth column it is in the bottoms. In all columns the pressure of the column is regulated by controlling the coolant flow in the condenser. Changes in the coolant flow change the amount of vapor in the column, thus changing the pressure. The most important difference in the control that follows this, is the flow controlled by the temperature controller. In the first three columns the temperature controller adjusts the outflow of the distillate. This way the control system is directly controlling the distillate product composition. In column 4 the

bottoms product composition is more important, in this column the temperature controller adjusts the outflow of the bottoms. The liquid level in the first three columns is regulated by controlling the outflow of the bottom product, whereas this controller adjusts the coolant flow in the reboiler for the last column. The flow from the reflux drums to the column of the first three distillation columns is controlled by the level controller on the reflux drum. In the fourth column this is controlled by a separate flow controller on the pipe leading back into the reactor. Finally, the flow of the superheated steam in the reboiler of the first three columns is controlled by a flow controller on the pipe where the steam flows into the reboiler.

The vents present in column 1 and 3 are controlled by the distillate outflow, because 0.1% of the distillate flow has to be purged to accommodate for the incondensable gasses. All columns have been fitted with several temperature indicators to be able to view the conditions inside the column. The makeup flow of ethylene glycol into the extractive distillation column is controlled by a flow indicator on the ingoing line of the solvent. This way the amount of solvent going into the column is always constant, independent on the recycle stream flow rate.

The pipes between the columns all have a flow and an analysis indicator, to monitor the composition and the feed to the next column. All pumps have an identical backup pump, so in case of pump failure, the process can still continue by using the backup.

After HAZOP

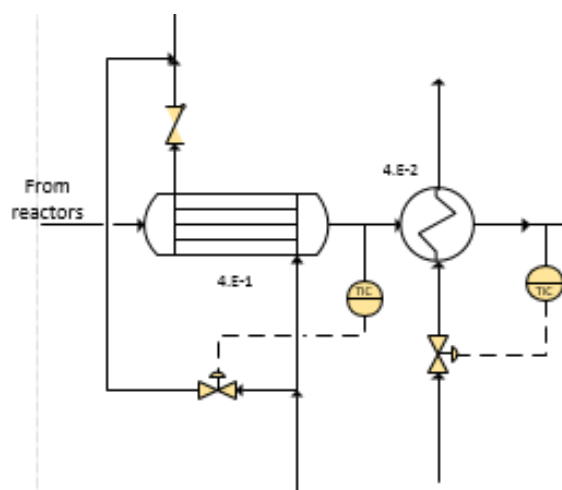


Figure 41: Control system feed pre-heaters

After performing the HAZOP, it became clear that several more control system were needed. These changes are marked yellow in the P&ID. Both the P&ID and the HAZOP analysis can be found in the appendices. The two feed preheaters need to be controlled to ensure the feed of

the work-up section is at the correct temperature. For the first heat exchanger direct flow control of the flows is not an option, because the flowrate is controlled elsewhere in the system. For this reason a bypass is installed, this will ensure correct temperatures. The second feed preheater is controlled by adjusting the flow rate of the steam. The tank containing the ethylene glycol is fitted with a level indicator with a low level alarm, to ensure there is always enough solvent in the system. If the amount of solvent would be too low, the purity of the product could decrease. The level indicator controllers of all columns have been fitted with a high and low alarm, to prevent the column from drying out or a change in product purity in case of failure elsewhere in the system. All columns are also fitted with a pressure relief valve to the gas disposal system to ensure no excessive pressure buildup in case of a failure in the system. To ensure no harmful gases are vented to the atmosphere, all gases coming from the vents on the reflux drums will go to the gas disposal system.

Chapter IV - EQUIPMENT SPECIFICATION

Syngas Cleanup

Tar reformer

The residence of the tar reformer was taken as 10s.⁴¹ Multiplying this with a gas flow rate 750 m³/s results in a total volume required of 7500 m³.

Fixed bed reactor

The total volume of the fixed bed reactors was determined by dividing the gas flow rate of 1101290 m³/h with an assumed space velocity of 5000 h⁻¹. This results in a total reactor volume of 220 m³/h. Taking a design spec of 20% into account gives a total reactor volume of 264 m³.

CSTR

The volume and residence time of the CSTR is calculated by hand using an absorption rate of 0.1 mol s⁻¹ m⁻². This value is obtained by extrapolation.⁴² The total reaction area is found by the following equation:

$A = \frac{F_{a,in}}{J_a}$ where $F_{a,in}$ is taken as the total molar flow rate (mol/s) of NO and SO₂ combined, J_a is taken as the absorption rate. By taking $F_{a,in} = 27.8$ mol/s and $J_a = 0.1$ mol s⁻¹ m⁻² results in a total reaction area of 278 m².

The area and volume of a single CSTR was taken from Alibaba where area and volume are 10 m² and 77 m³ respectively. Increasing the total area by approximately 10% results in a total of 30 CSTRs. According to the Aspen model the total gas flow rate and liquid flow rate coming in are 348726 m³/h and 32.7 m³/h respectively. Recalculating this to m³/s results in a gas and liquid flow rate of 3.33 m³/s and 0.01 m³/h. This results in a gas and liquid residence time of 0.77s and 275s respectively.

Pumps

The pump type chosen for this process is the positive displacement pump. A positive displacement pumps liquid in separate units. The concentrations in the CSTR must have a specific value for optimum absorption. By using positive displacement pumps no control valves are necessary. The pumps can be controlled directly for transporting the right quantity of solution.

To keep the pressure difference low, a flowrate of 100 m³/h with dP = 1 bar was used.

The pumps transport $60 \text{ m}^3/\text{h}$ with a pressure of 10 barg.⁴³ Three different pump systems are made to transport $500 \text{ m}^3/\text{h}$ each. This results in 15 pumps, excluding 6 spare pumps.

Tanks

The volume of the tank was determined by assuming a capacity for a day. Multiplying that with $500 \text{ m}^3/\text{h}$ of flow from each tank results in a volume of 12000 m^3 .

Nitrogen Membrane filters

One filter system requires a feed air of $868 \text{ Nm}^3/\text{h}$ and an inlet pressure of 10 barg.⁴⁴ According to Aspen the feed gas flow rate is $343202 \text{ m}^3/\text{h}$. Dividing that with $868 / 10 = 86.8 \text{ m}^3/\text{h}$ results in a total of approximately 4000 filter systems.

Heat exchangers

The total exchange area was obtained from the Aspen model.

Material of Construction (MoC)

For all equipment that is not in contact with corrosive material 316L or SS316 is used. To improve the strength of the heat exchanger tubes, 316LW is chosen as material. 316LW is the welded version of 316L. The tubes need to be strong due to a pressure difference of 9 bar. To contain a temperature of 1500°C in the tar reformer insulation material is necessary. The same holds for the furnace. For both ceramic foam (Al_2O_3) is used. The equipment that is in contact with the corrosive sodium hydroxide is made from Monel, except for the sodium hydroxide pumps which are made from Carpenter 20. Monel and Carpenter 20 are both nickel alloys. The nickel alloys are highly resistant to corrosive materials.

Equipment Code	Title	Capacity (m ³ /h) V (m ³ /h) *	Pressure (bar)	Temperature (°C)	Duty (kW)	MOC	Dimensions
1.E-1	Heat exchanger (Shell and tube)	0.70e06	10	Hot fluid outlet: 20°C	392585	Tube: 316LW, Shell: 316L	7160.72 m ²
1.E-2	Heat exchanger (Shell and tube)	1.10E06	1	Hot fluid outlet: 37-50 °C	750434	Tube: 316LW, Shell: 316L	46275 m ²
1.E-3	Heat exchanger (Shell and tube)	2.00E06	1	Hot fluid outlet: 650-760 °C	984956	Tube: 316LW, Shell: 316L	45050.2 m ²
1.E-4	Furnace	1.00E06	10	Gas outlet: 1500-1800 °C	1039499	SS 316, Insulation: Ceramic foam (Al ₂ O ₃)	-
1.E-5	Heat exchanger (Shell and tube)	0.80E06	10	Hot fluid outlet: 40 °C	443252	Tube: 316LW, Shell: 316L	27060 m ²
1.E-6	Heat exchanger (Shell and tube)	0.33E06	10	Hot fluid outlet: 37 °C	21971	Tube: 316LW, Shell: 316L	2076 m ²
1.K-1	Compressor	5,00E+05	10	20 °C	3992285	SS 316	-
1.K-2	Compressor	5,00E+05	10	37-50 °C	437787	SS 316	-
1.K-3	Compressor	2562	20	-	758	SS 316	-
1.P-1/P-2/P-3	Positive displacement pump	100	dP=0	20 °C	-	SS 316/Carpenter 20/Carpenter 20	-
1.S-1	Cyclone	1.2 Mton/year syngas	1	20 °C	-	SS	r = 0.25, H = 1 [C]
1.S-2	Demister	3.54E06	1	37-50 °C	-	SS 316	-
1.S-3	Nitrogen membrane filter	198	10	37-50 °C	-	SS 316	1.625*0.812*2.286
1.V-1	Tar reformer	2.7E06	10	1500-1800 °C	266715	SS 316, Insulation: Ceramic foam (Al ₂ O ₃)	r = 5.0, H = 50 [C]

1.V-2a/b	Fixed bed reactor a/b	60 kmol/h H ₂ S	10	650-760 °C	2713/10088	316L	r = 0.875, H = 4.5 [C]
1.V-3	CSTR	108 kmol/h (NO+SO ₂)	1	37-50 °C	-690	Monel	r = 1.75, H = 8.0 [C]
1.V-4	Nitrogen storage vessel	500	20	20 °C	-	SS 316	r = 4.0, H = 10 [C]
1.V-5	SO ₂ neutralization vessel	500	1	20 °C	-	SS 316	r = 4.0, H = 10 [C]
1.T-1	0.2M KMnO ₄ solution storage tank	500 (0.2M)	1	20 °C	-	SS 316	r = 1.25, H = 25 [C]
1.T-2	2M NaOH solution storage tank	500 (2M)	1	20 °C	-	Monel	r = 1.25, H = 25 [C]

Table 24: Syngas processing equipment specifications

*Capacity given in m³/h or m³, which is dictated by the object discussed. For example, a pump's capacity value is obviously in m³/h, but a tank's capacity is of course in m³.

Growth/acidogenesis reactor (R1)

Equipment specs must be chosen with safety in mind, with consideration to the design parameters, MOC, and room for error accepted. An overview of the equipment specifications, as referred to in the P&ID, are listed in **Table 25**. Next, an overview the design approach for each type of equipment takes place.

Equipm ent Code	Title	Capacity (m3) V (m3/h) *	Pressure (bar)	Temperat ure (°C)	Duty (kW)	MOC	Dimensions	Comment
2.E-1	Internal cooling Coil - Growth Reactor	1400	1	18-37	30700	SS316L	A = 1800 m2	Area refers to surface area of bare coil needed.
2.P-1	Acid Pump	72	1-10, dp=9	25		SS316	-	Reciprocating positive displacement pump
2.P-2	Base Pump	72	1-10, dp=9	25		SS316	-	Reciprocating positive displacement pump
2.P-3	Nutrient Stock Pump	62	1-10, dp=9	25		SS304	-	
2.P-4	Water Pump (Growth Reactor)	1000	1-10, dp=9	25		SS304	-	
2.P-5	2.V-1 Medium pump	1030	10, desired dp = 0	37		SS304	-	Pumping Medium from Growth to Production Reactor
2.S-1 ⁴⁵	Syngas org- material filter x 50	6700	10	37	-	Polytetra fluoroeth ylene membran e	r = 0.07, H = .25 [C]	(Area per filter = 0.88m^2) Total area = 44m^2
2.T-1	2M HCl storage	806	1	25	-	SS904L	r = 4.41, H = 13.21 [C]	
2.T-2	2M HCl storage	806	1	25	-	SS904L	r = 4.41, H = 13.21 [C]	
2.T-3	Nutrient Storage tank.	1700	1	25	-	SS304	r = 7.81, H = 8.85 [C]	@ max Vol. capacity leaves 1 m head (only needs 1700)
2.T-4	Antifoam 204 tank	11	1	25	-	SS304	r = 1.5, h = 1.62 [C]	@max Vol. leaves 0.15m head space. (only needs 10m3)
2.T-5	Water reservoir (x 5)	2500	1	25	-	SS304	r = 9.3, H = 10.0 [C]	@max Vol. leaves 0.75m head space (only need 2500x5 - total capacity = 12500m ³)
2.V-1	Growth Reactor (stirred)	900	10	37	-	SS304	r = 3.54, H = 23 [DC]	@ max leaves 1.8m heat room (needs 830m3)
2.V-2	Non cooled flasher/Pressure changer	Volume = 0.9 Flow = 3150	10-1, dp = -9	20	144.8	SS304	r = 0.3, H = 3 [DC]	Used Souders Formula
2.V-3	Cooled Flasher/ 1 bar	Volume = 31, Flow = 66500	1	10	340.4	SS304	r = 1.2, H = 6 [DC]	Used Souders Formula

Table 25: Equipment list with specifications – Growth Reactor Setup

*Capacity given in m³/h or m³, which is dictated by the object discussed. For example, a pump's capacity value is obviously in m³/h, but a tank's capacity is of course in m³.

Note the dimension syntax used in **Table 25** is shown in **Table 26**.

Dimensional Footnotes			
Footnote	Object	Syntax	Specify
R	Rectangular	(LxWxH)	L W H
C	Cylindrical	(pi*r^2) * H	R H
DC	Domed Cylinder (Hemispherical)	(pi*r^2) * H + 4(pi)r^2	R H

Table 26: Dimensional syntax

For each equipment, a MOC is chosen. MOC is not extensively elaborated on, but is always stainless steel, and varies between stainless steel 304 (ss304), or stainless steel 316L (ss316L), and stainless steel 904L (ss904L)⁴⁶. All alloys are resistant to acids and bases in the conditions used in this system, but ss316 is slightly more acid and base resistant than ss304, and less prone to pitting. Stainless steel 316L is therefore applied in more harsh applications in the system such as the acid base pumps, or heat exchanger, but ss304 is sufficient, and used almost everywhere else. This decision is also done to minimize costs, as ss304 is a readily used alloy, and can therefore be readily acquired. Lastly stainless steel 904L is used for the acid and base tanks, as this alloy is made to resist the entire pH range.

Heat Exchanger

As per Aspen, the cooling required for the growth reactor is 30MW, and a bare coil heat exchanger was chosen to deliver this cooling. The heat exchanger was chosen to have a MOC of stainless steel (ss316L). According to Aspen, a flow rate of 1400 m³/h at 18°C water was required to maintain a maximum of 37°C in the reactor. To determine the surface area of the cooling coil, a heat transfer equation was used.

$$Q = UA\Delta T \quad 47$$

Q = heat loss [W]

U = heat transfer coefficient [W/(m² K)]

dT = Temperature change [K]

Equation 26: Heat Transfer Equation

Using **Equation 26**, and a U of 1000 W/(m² K)⁴⁸, and a dT of 17K, an area of 1800m² contact area.

Tanks

Design of tanks was fairly straight forward. The tanks were sized to provide the system with one day of supply in the case nutrient flow, and 12h in the case of water flow. The design pressure and temperature is 1 bar and 25°C. These tanks are constructed of ss304, apart from the acid and base tanks, that were made of ss904L. The acid and base tanks were sized to provide a significant pH change to the reactor system and provide base and acid to both reactor 1 and 2, though this is not shown in PID. To supply a large excess of acid or base, the acid and base tanks were sized to account for 5% of the large reactor volume. For economical purposes, two sets of acid and base tanks are constructed to supply all reactors, and therefore each supply accounts for 25% of the large reactor 2 volume, or 1612m³. Since both the growth tank and production tank have their own acid and base supply, the total 1612m³ of acid and base specified is split between the reactors. The acid and base tanks in the growth reactor section therefore total 806.0 m³ each. Their design pressure and temperature is 1 bar and 25°C, and they're made of ss316L to provide extra protection against the acidic and basic environment.

The nutrient and water tanks are sized a 1:2 height:diameter ratio, to keep a wide base and shorter height. An additional 1 m of head space is also accounted for, and the nutrient tank came to a volume of 1700m³ with a radius of 7.81m and height of 8.85m. The acid and base tanks were designed similarly, and have a radius of 4.41m, and height of 13.21m.

Vessels

The only vessel that is not a flasher in the growth reactor setup is the main reactor. This reactor is sized similarly to a bubble column, at a 3:1 height:diameter ratio. This is because syngas is bubbled through the column, so gas residence time should be optimized and similar CSTRs that use gas feeds have said ratio. This resulted in a reactor radius of 3.54m, and height of 23m. This also accounted for a 1.8 m head space. The design pressure and temperature of the reactor was 10bar and 37°C. The MOC used is ss304.

Flashers

Two flashers exist in the current setup, one of which induces a pressure change on the gas flow of 9 bar without cooling, and the second of which cools the outlet syngas to condense any remaining ethanol or acetate. Both flashers are made of stainless steel 304, and as per aspen accept 3150m³/h (2.V-2, 20°C, 10bar-1bar) and 66500 m³/h (2.V-3, 10°C, 1bar). Using Aspen, the duty per flasher was calculated at 144.8kW and 340.4 kW resp. To determine the size of

the flashers, Sounders-Brown theory was used. Sounders-Brown theory states that for a flasher to achieve reasonable separation, the internal velocity must be within a bound. If one determines the internal velocity of a flasher, and the volumetric inflow is known, one can solve for the cross-sectional of said flasher. Sounders-Brown equation provides empirical derived velocity values k , that are a function of the internal flasher velocity V , and are empirically determined for different types of flashers and flasher heights.

$$V = (k) \sqrt{\frac{\rho_L - \rho_v}{\rho_v}}$$

V = maximum allowable vapor velocity (m/s)

ρ_L = liquid density

ρ_v = vapor density

k = empirically determined allowable velocity

Equation 27: Sounders-Brown Equation⁴⁹

Using an empirically derived k value of 1.3 for flash distillation, and densities provided for the syngas stream from Aspen, the sizing of the flashers resulted in two cylindrical tanks, with a radius of 0.3m and height of 3m for flasher 1 (2.V-2, 20°C, 10bar-1bar), and radius of 1.2m and height of 6m for flasher 2 (2.V-3, 10°C, 1bar).

Pumps

The water and nutrient pumps as well as the media pump after reactor 1 was designed to supply a steady state flow as determined via the flow calculator in excel. Most pumps use a MOC of ss304, but the acid and base pumps use ss316, and a design temperature of 25°C for supply pumps and 37°C for reactor media pump. All supply pumps are rated for a 100m pressure head, though under running conditions only need a 90m head. The acid and base pumps were designed to deliver near 10% of the reactor 1 volume within 1 hour, a volume that would significantly change pH. This resulted in a flow need of near 72m³/h. The nutrient volumetric flow needs a steady state 58m³/h, and is rated for 62m³/h. Finally, the water inlet needs 920 m³/h capacity, but is rated for 1000 m³/h.

Filtration

The filters used for syngas cleaning are 3nm high-flow membrane filters with polytetrafluoroethylene membranes. The membrane filters are rated to remove bacteria, and should work to remove organic matter taken out of the reactor by the out-flowing syngas. The filters are sold by Emflon⁴⁵, and each have a surface area of 0.88m². According to calculations based on rated flow speeds through the membrane filter, 47 filters are needed, so 50 filters will be used in reality. This totals a surface area of 44m² of membrane.

Production/solventogenesis reactor (R2)

In the following sections, crucial specification pertaining to the major equipment used in the solventogenesis reactor section can be found listed, along with brief explanations on important reasoning behind some the decision. For the specific nomenclature of the equipment, please refer to **Figure 31**.

Vessel(s)

A few important point of consideration regarding the specification of vessels, especially pressure vessels, include its operating pressure, temperature, and pH. The said vessel specification simply have to met all of the aforementioned requirements. Regarding pressure, another crucial point of consideration is the geometry of a vessel. Generally, vessels with more welded joints and edges will be much more prone to stress cracking regardless of its materials of construction (MoC). This is owing to the so-called tip effect, which concentrates and amplify stress on a pointy end, thus leading to premature failure. To circumvent the issue with stress cracking, often additional material would need to be used on the said pointy ends, thus increasing the overall cost of the material needed to build the vessel. Alternatively, one can consider a vessel geometry with as little pointy end as possible, implying a sphere being the most ideal geometry. Sphere however, raises another point of discussion, since it is a shape bearing the highest surface area-to-volume ratio, which economically, is a quantity one would like to minimize in the case of building vessels. A compromise would then be, for example, a cylindrical vessel with domed hemispherical heads, which would be able to better handle pressure, relative to that of prismatic or flat headed cylindrical vessels. In the case of 3.V-1, however, as it is a bubble column, an additional important point of consideration is its height-to-diameter ratio when determining the dimensions of the said vessel. For instance, in the case of 3.V-1, a relatively high ratio of 6 was chosen to provide a reasonable bubble rise time,

whereas in the case of 3.V-2, a very much lower ratio of 1.5 was used to further minimize material cost of the vessel.

As for a vessel's MoC, it is important to simultaneously consider a material that is compatible with the content and process occurring within the vessel, while also keeping in mind cost consideration and the material's physical property. For most cases, where mild conditions were to be involved, stainless steel, especially SS304 alloy, is one of the most commonly used MoC, owing to its wide range of compatibility and relatively cheap price. Following this section, the specifications for the two vessels, 3.V-1 and 3.V-2, can be found.

3.V-1

Type	: Reaction pressure vessel
Function	: Microbe catalyzed fermentation reaction
MoC	: Stainless steel (SS304)
Operating P	: 10 bar
Operating T	: 35°C
Operating pH	: 4.4-4.8
Geometry	: Cylindrical vessel, hemispherical heads, vertical
Reaction volume	: 3500 m ³
Dimensions	: 54.32m x 9.05m (H x D)

3.V-2

Type	: Pressure vessel
Function	: Liquid outlet stream pressure relief flasher from 10 bar to 1 bar (atmospheric)
MoC	: Stainless steel (SS304)
Operating P	: 10 bar
Operating T	: 35°C
Operating pH	: 4.4-4.8
Geometry	: Cylindrical vessel, hemispherical heads, vertical
Operational volume	: 500 m ³
Dimensions	: 11.27m x 7.51m (H x D)

Tank(s)

Much like pressure vessels, a tank or storage tank is essentially an atmospheric vessel. Therefore, similar points should also be considered pertaining to the design specification of storage vessels/tanks. Since pressure, in the case of atmospheric storage vessels, are less of an issue, flat-headed cylindrical geometry can be used as it results in the least amount of surface area possible in the case of cylindrical vessels. For the same reason mentioned earlier for pressure vessels, a height-to-diameter ratio of 1.5 was also used in sizing all of the storage vessels.

Regarding its MoC, much like the pressure vessels, the same applies for storage tanks. A material that is compatible with the content and function of the vessel has to be considered, while also keeping in mind the cost of the material and its physical property. For instance, in the case of 3.T-1 and 3.T-2, where high concentration acid and base, respectively, have to be contained, a special alloy of stainless steel, SS904L was chosen, as the said alloy was specifically designed to withstand such harsh condition. Following this section, the specifications for the storage tanks can be found.

3.T-1

Type	: Storage vessel
Function	: Containment of aqueous NaOH 2M solution
MoC	: Stainless steel (SS304)
Operating P	: 1 bar (atmospheric)
Operating T	: 25°C (room temperature)
Operating pH	: 14
Geometry	: Cylindrical vessel, flat heads, vertical
Storage volume	: 806.0 m ³
Dimensions	: 13.21m x 8.81m (H x D)

3.T-2

Type	: Storage vessel
Function	: Containment of aqueous HCl 2M solution
MoC	: Stainless steel (SS304)
Operating P	: 1 bar (atmospheric)
Operating T	: 25°C (room temperature)

Operating pH	: 0.3
Geometry	: Cylindrical vessel, flat heads, vertical
Storage volume	: 806.0 m ³
Dimensions	: 13.21m x 8.81m (H x D)

3.T-3

Type	: Storage vessel
Function	: Containment of liquid outlet stream
MoC	: Stainless steel (SS304)
Operating P	: 1 bar (atmospheric)
Operating T	: 35°C
Operating pH	: 4.4-4.8
Geometry	: Cylindrical vessel, flat heads, vertical
Storage volume	: 3500 m ³
Dimensions	: 21.55m x 14.37m (H x D)

3.T-4

Type	: Storage vessel
Function	: Containment of water
MoC	: Stainless steel (SS304)
Operating P	: 1 bar (atmospheric)
Operating T	: 25°C
Operating pH	: 7
Geometry	: Cylindrical vessel, flat heads, vertical
Storage volume	: 806.0 m ³
Dimensions	: 13.21m x 8.81m (H x D)

Pump(s)

A few important point of consideration regarding the specification of pumps, include its operating flow rate, pressure differential, and temperature. Pumps that suitably met the specified requirements therefore have to be picked. The flow rate and pressure differential specification of a pump is simply determined by the process and the function the said pump

serves. It should also be noted that some of the pump need to be specified as variable flow rate speed-controlled pump, as some of them serves as a part of a controlled-addition system into the reactor. Based on these, a suitable pump can then be selected by using **Figure 42**, **Figure 43**, and **Figure 44** as a guideline. Similarly, its operating temperature is also determined by the function a pump serves. Much like what is described for the previous equipment, based on this temperature and function requirement consideration, the MoC for a pump can also be selected. Lastly, as it was mentioned in the previous sections, pump was used to symbolize transport universally, and that in any instance of gaseous component transportations, pump would then refer to a gas blower/fan equipment. The gas transport equipment refer to a fan specifically since virtually no pressure increase is required for the gases and only a gas flow is of necessity for the process. Following this section, the specifications for the pumps can be found.

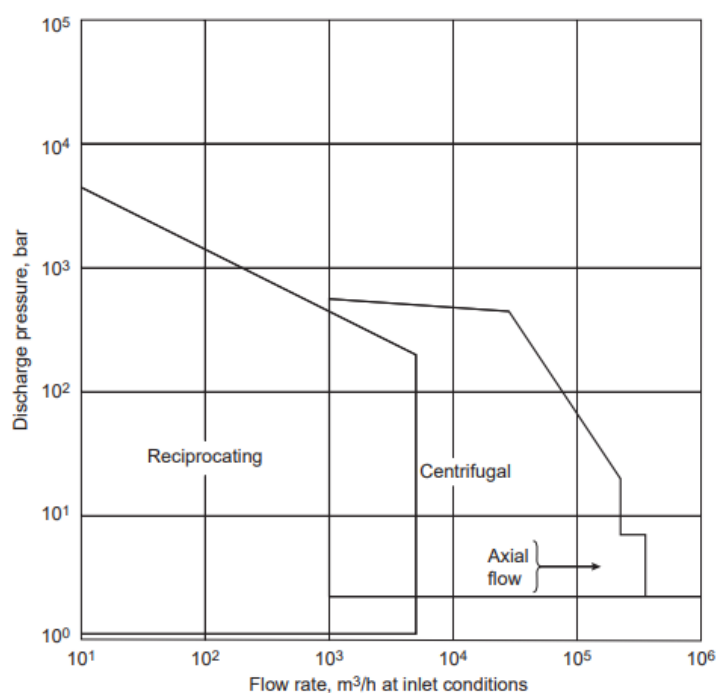


Figure 42. Gas compressor selection guide⁵⁰

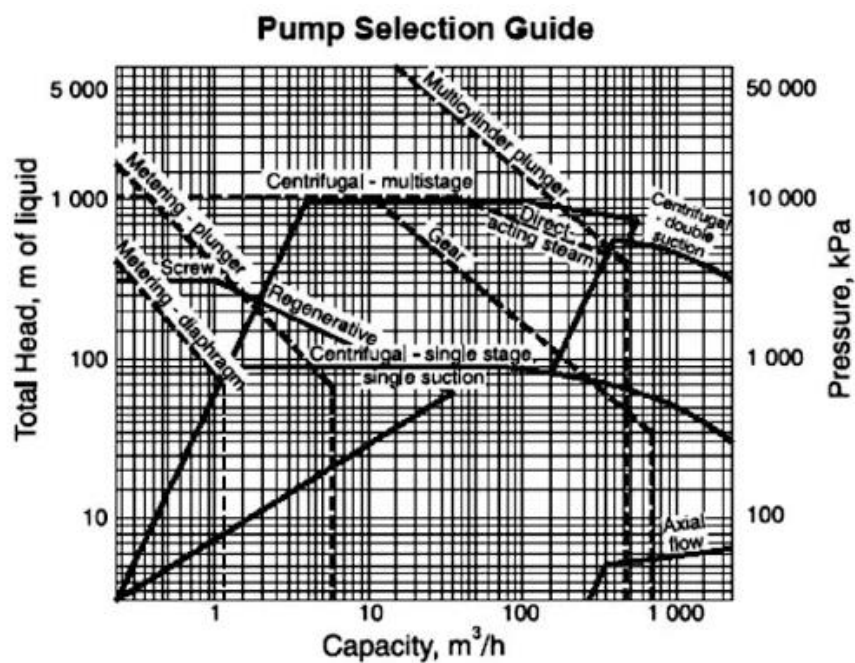


Figure 43. Liquid centrifugal pump selection guide⁵⁰

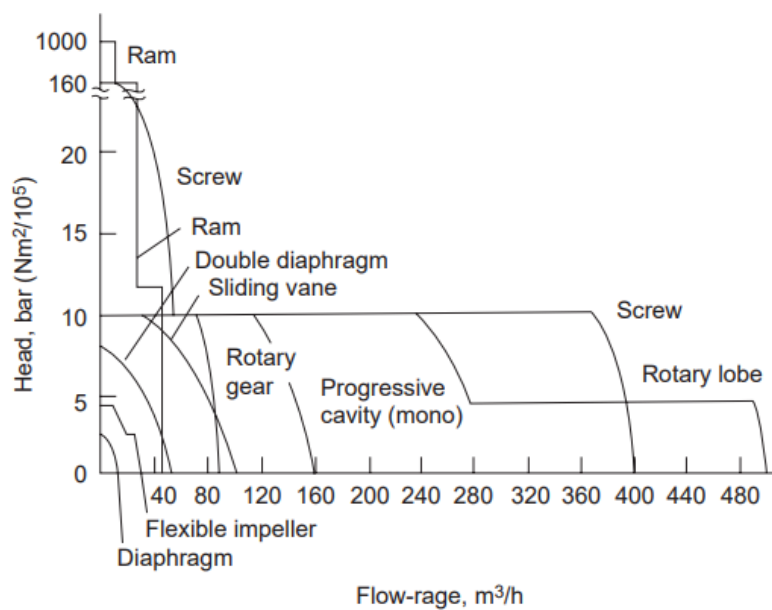


Figure 44. Liquid positive displacement pump selection guide⁵⁰

3.P-1 A/B

Type	: Dosing, positive displacement
Function	: Aqueous NaOH 2M transport
MoC	: Stainless steel (SS304)
Operating flowrate	: Variable
Operating dP	: 9 bar
Operating T	: 25°C (room temperature)
Operating pH	: 14

3.P-2 A/B

Type	: Dosing, positive displacement
Function	: Aqueous HCl 2M transport
MoC	: Stainless steel (SS304)
Operating flowrate	: Variable
Operating dP	: 9 bar
Operating T	: 25°C (room temperature)
Design T	: 40°C
Operating pH	: 0.3

3.P-3 A/B

Type	: Single stage centrifugal
Function	: Liquid outlet stream transport
MoC	: Stainless steel (SS304)
Operating flowrate	: 1200 m ³ /h
Operating dP	: -
Operating T	: 35°C
Operating pH	: 4.4-4.8

3.P-4 A/B

Type	: Single stage centrifugal blower/fan
Function	: Gas inlet stream transport
MoC	: Stainless steel (SS304)
Operating flowrate	: 5000 m ³ /h
Operating dP	: -

Operating T : 35°C
 Operating pH : -

3.P-5 A/B

Type : Dosing, e.g. PWM fan, reciprocating positive displacement fan/blower
 Function : Gaseous H² transport to inlet stream
 MoC : Stainless steel (SS304)
 Operating flowrate : 17500 m³/h
 Operating dP : -
 Operating T : 35°C

3.P-6 A/B

Type : Dosing, positive displacement
 Function : Water transport
 MoC : Stainless steel (SS304)
 Operating flowrate : Variable
 Operating dP : 9 bar
 Operating T : 25°C (room temperature)
 Operating pH : 7

3.P-7 A/B

Type : Dosing, positive displacement
 Function : Antifoam 204 transport
 MoC : Stainless steel (SS304)
 Operating flowrate : Variable
 Operating dP : 9 bar
 Operating T : 25°C (room temperature)
 Operating pH : -

Heat exchanger(s)

While the general temperature, pressure, and operating pH of the heat exchanger in the case of R2 follows from that of the vessel specification itself as the heat exchanger was specified as an internal cooling coil, another important design specification for heat exchanger is its exchange area. The exchange area can be obtained using the previously mentioned cooling duty and temperature difference values obtained from the simulation done in Aspen Plus V8.6, along with **Equation 28**, and with an overall heat transfer coefficient assumed to be $1000 \text{ W/m}^2\text{K}$, for liquid-to-liquid exchange through a tubular metal interface⁵¹.

Equation 28 $Q = UA\Delta T$

Pertaining to its MoC, while its requirement is similar to that of the vessel its located in, an SS316L alloy was chosen instead as the equipment, being a heat exchanger, will be more likely to be exposed to events, such as local hot spots and rapid cooling and heating cycles. Following this section, the specifications for the said heat exchanger can be found.

3.E-1

Type	: Internal cooling coil
Function	: Temperature control of R2
MoC	: SS316L
Operating flowrate	: $18000 \text{ m}^3/\text{h}$
Operating Q	: 400MW
Operating P	: 10 bar
Operating T	: 35°C
Exchange area	: 23000 m^2

Filter(s)

Again, the general requirements, such as temperature and operating pH of the filter in the case of R2 follows from that of the reactor vessel specification itself, as the filter would have to handle the liquid outflow from the said reactor, which based on its CISTR-like behavior, would have the same outlet conditions as it is inside the reactor. Additionally, for filters other point of consideration would be the flowrate the said filter should be able to handle, and its material compatibility with the said liquid medium, along with the pore size. Pore size is particularly important and have to be based on the level of separation one is trying to achieve. For example,

in the case of cell filters, a size of 0.4 μm would suffice, as the microbes of interest, assuming rod-like shape, have on average, a diameter of 1 μm and length of over 2 μm . As for its MoC, it is also dependent on the aforementioned pore size, as not all materials can be manufactured to have the desired pore size. While pertaining to its flow rate capacity, if a single filter will not suffice, parallel installation of filters, thus making them a module of a filter can be used to accommodate the desired flow rate. Following this section, the specifications for the said cell filter can be found.

3.S-1 A/B

Type	: Hollow fiber membrane filter module of 130 individual filters
Function	: Solid-liquid separation of cell mass and liquid outlet stream suspension
MoC	: Polysulfone
Operating flowrate	: 650 m^3/h
Operating dP	: -
Operating T	: 35°C
Max. solid concentration	: -
Operating pH	: 4.4-4.8
Pore size	: 0.4 μm
Geometry	: Cylindrical, vertical

Product Work-up

In this section the equipment and their sizes of the work-up section of the project will be specified. Each type of equipment will be discussed and calculations will be explained. Under each section, the equipment list with the equipment code corresponding to the P&ID is shown. The material of construction for all equipment in this section will be stainless steel grade 304, because this material is appropriate for the temperatures, pressures and compounds used in this system.⁵²

Distillation columns

The size of the extractive distillation column follows directly from the aspen model, from the rate-based simulation method. This is not the case for the other three columns, since they use the equilibrium calculation method. The diameter and the height of the column are calculated

separately. Detailed calculations were done for column 1 and 2. The formulas will be discussed below. The final design resulting from sizing and the Aspen model can be found in **Table 27**.

For the height of the column, first the number of real plates is required. This can be calculated from the plate efficiency, which can be obtained from O'Connell's correlation⁵³:

$$E_0 = 51 - 32.5 \log(\mu_a \alpha_a)$$

$$E_0 = \frac{\text{number of theoretical stages}}{\text{number of real plates}}$$

E_0 = plate efficiency

μ_a = molar average liquid viscosity (mPa*s)

α_a = average relative volatility of the light key

The average relative volatility can be calculated by dividing the vapor pressure of the light key (ethanol) by the vapor pressure of the mixture entering the column. Both values for the vapor pressure can be obtained from Aspen. Once the number of real plates is known, the total height of all the plates can be calculating by multiplying the number of plates by the plate spacing. Finally, some extra height has to be added to accommodate for the condenser and the reboiler. For simplicity, one meter was added for both. The location of the feed plate was adjusted to the new number of plates by multiplying by the ratio of the new number of plates and the original number of stages.

For the height calculation, Towler's book⁵³ states formulas based on the Souders and Brown equation:

$$\hat{u}_v = (-0.171l_t^2 + 0.27l_t - 0.047) \left[\frac{\rho_L - \rho_v}{\rho_v} \right]^{1/2}$$

$$D_c = \sqrt{\frac{4V_w}{\pi\rho_v\hat{u}_v}}$$

\hat{u}_v = maximum allowable vapor velocity (m/s)

l_t = plate spacing (m)

ρ_L = liquid density (kg/m³)

ρ_v = vapor density (kg/m³)

D_c = column diameter (m)

V_w = maximum vapor rate (kg/s)

All values required by these formulas follow from the Aspen model. To keep the dimensions of the columns reasonable, the choice was made to use several parallel columns where the diameter of the column exceeded four meter. For column 1 this means 6 parallel columns are required and for column 2 three parallel columns. Columns 3 and 4 both stay within the mentioned boundary. The feed mass flows, the condenser and reboiler duty have been adjusted to account for the parallel columns. This changes the process parameters obtained from the aspen model in the process design section. The updated values obtained from the sizing calculations can be found in **Table 27**.

	Column 1	Column 2	Column 3	Column 4
number of parallel columns	6	3	1	1
feed mass flow (kg/h)	184003	76458	98516	98516
diameter (m)	3,88	3,99	4	3,89
number of plates	18	35	40	15
plate spacing (m)	0,6	0,6	0,6	0,6
plate type	sieve	sieve	sieve	sieve
feed plate	13	26	32	11
pressure (bar)	1	1	1-3,2	1
height (m)	12,8	23	26	11
reflux ratio	1	5	3	2,15
boilup ratio	0,5	2	2	0,6
condenser duty (kW)	-37389	-53806	-88415	-14916
reboiler duty (kW)	45280	54736	98207	14402
solvent mass flow (kg/h)	-	-	100000	-
solvent feed plate	-	-	6	-

Table 27: Final design parameters makeup section

Equipment Code	Title	Capacity (m ³) V (m ³ /h)	Pressure (bar)	Temperature (°C)	Duty (kW)	MOC	Dimensions
4.C-1	Distillation column	187	1	80-100	-	SS304	D = 3.88, H = 12.8
4.C-2	Distillation column	90	1	70-100	-	SS304	D = 3.99, H = 23.0
4.C-3	Extractive distillation column	130	1-3.5	70-200	-	SS304	D = 3.00, H = 26
4.C-4	Solvent recovery column	114	1	100-200	-	SS304	D = 3.89, H = 11

Table 28: Equipment list distillation columns product work-up

Heating/cooling equipment

To calculate the exchange area of the heating and cooling equipment in the work-up section, the following formula was used⁵³:

$$Q = A * U * \Delta T$$

Q = heat transferred per unit time (W)

A = heat transfer area (m²)

U = overall heat transfer coefficient (W/(m² * °C))

ΔT = temperature difference (°C)

Both the formula and the values for the overall heat transfer coefficient were obtained from Towler's book⁵³. The condensers of all columns were modelled as air cooled heat exchangers. The air was assumed to be at atmospheric conditions (20 °C and 1 bar). The reboilers of the distillation columns were modelled as kettle reboilers. The feed pre-heaters were modeled as shell and tube heat exchangers. For the reboilers and the second feed pre-heater, the hot stream was assumed to be superheated steam at 250 °C.

Equipment Code	Title	Capacity (m ³) V (m ³ /h)	Pressure (bar)	Temperature (°C)	Duty (kW)	MOC	Dimensions	Comment
4.E-1	First feed pre-heater	105/1127	1	20-200	40536	SS304	A = 169	Shell and tube
4.E-2	Second feed pre-heater	1127	1	26-60	8969	SS304	A = 737	Shell and tube
4.E-3	Column 1 condenser	45	1	81	37387	304LW	A = 1226	Air cooler
4.E-4	Column 1 reboiler	79	1	100	45279	SS304	A = 121	Kettle reboiler
4.E-5	Column 2 condenser	217	1	72	53808	304LW	A = 2070	Air cooler
4.E-6	Column 2 reboiler	95	1	100	54737	SS304	A = 146	Kettle reboiler
4.E-7	Column 3 condenser	368	1	73	88415	304LW	A = 3336	Air cooler
4.E-8	Column 3 reboiler	227	1	193	98207	SS304	A = 2297	Kettle reboiler
4.E-9	Column 4 condenser	18	1	99	14917	304LW	A = 472	Air cooler
4.E-10	Column 4 reboiler	63	1	197	14402	SS304	A = 362	Kettle reboiler

Table 29: Equipment list heat exchangers product work-up

Pumps

The equipment specifications for the pumps in the work-up section are below. The values for the temperature and capacity were taken from the Aspen model.

Equipment Code	Title	Capacity (m ³) V (m ³ /h)	Pressure (bar)	Temperature (°C)	Duty (kW)	MOC	Dimensions	Comment
4.P-1 a/b	Column 1 condenser pump	45	1	81	-	SS304	-	Centrifugal pump
4.P-2 a/b	Column 2 condenser pump	217	1	72	-	SS304	-	Centrifugal pump
4.P-3 a/b	Solvent pump	94	1	20	-	SS304	-	Centrifugal pump
4.P-4 a/b	Column 3 condenser pump	368	1	73	-	SS304	-	Centrifugal pump
4.P-5 a/b	Column 4 feed pump	114	1	193	-	SS304	-	Centrifugal pump
4.P-6 a/b	Column 4 condenser pump	18	1	99	-	SS304	-	Centrifugal pump
4.P-7 a/b	Solvent recycle pump	94	1	197	-	SS304	-	Centrifugal pump

Table 30: Equipment list pumps product work-up

Tanks

The size of the solvent tank was assumed to be large enough to last for one hour of fresh ethylene glycol feed. In reality, almost all of the solvent is recycled, so most of the tank contents

will be used as a make-up feed. The reflux drums in the columns were sized with a hold-up time of 10 minutes in mind⁵³. This means the flowrate per hour was divided by 6 to obtain the hold-up time per 10 minutes. The dimensions of the tanks were obtained from the Aspen Process Economic Analyzer, which give the economically optimal dimensions.

Equipment Code	Title	Capacity (m ³) V (m ³ /h)	Pressure (bar)	Temperature (°C)	Duty (kW)	MOC	Dimensions	Comment
4.T-1	Column 1 reflux drum	7,5	1	81	-	SS304	D = 1.5, L = 4.24	Horizontal drum
4.T-2	Column 2 reflux drum	36	1	72	-	SS304	D = 2.5, L = 7.33	Horizontal drum
4.T-3	Solvent tank	100	1	20	-	SS304	D = 4.5, H = 6.29	Vertical storage tank
4.T-4	Column 3 reflux drum	61	1	73	-	SS304	D = 3, L = 8.63	Horizontal drum
4.T-5	Column 4 reflux drum	3	1	99	-	SS304	D = 1.2, L = 2.65	Horizontal drum

Table 31: Equipment list tanks product work-up

Chapter V - COST ANALYSIS AND CONCLUSION

Equipment Cost

Note: To determine the costs of the equipment used, some equipment specifications were determined, and then run through Aspen Process Economic Analyzer⁵⁴ (V8.7.1).

Syngas processing

These are the costs according to the previously mentioned equipment specifications.

Equipment Code	Estimated Cost (\$)	Quantity	Total cost (\$)
1.E-1	2282400	4	9.129.600,00
1.E-2	14681800	13	190.863.400,00
1.E-3	14289600	24	342.950.400,00
1.E-4	1013700	1	1.013.700,00
1.E-5	8578500	1	8.578.500,00
1.E-6	674000	5	3.370.000,00
1.K-1	66379798,86	7	464.658.592,00
1.K-2	66379800	1	66.379.800,00
1.K-3	1057700	1	1.057.700,00
1.P-1/P-2/P-3	16850	21	353.850,00
1.S-1	14000	500	7.000.000,00
1.S-2	155000	1	155.000,00
1.S-3	1.203	4000	4.812.000,00
1.V-1	4277300	4	17.109.200,00
1.V-2a/b	1555000	50	77.750.000,00
1.V-3	464700	30	13.941.000,00
1.V-4	205640	5	1.028.200,00
1.V-5	205640	4	822.560,00
1.T-1	2704600	1	2.704.600,00
1.T-2	9785500	2	19.571.000,00
Total:			1.233.249.102,00

Table 32: Syngas processing costs

Growth/acidogenesis reactor (R1)

Equipment costs largely pertain to the sizing, capacity, and MOC used to design each piece of equipment. An overview of the total equipment costs for all five parallel plants for the growth stage alone, and all equipment referred to in the P&ID of the growth stage, are listed in **Table 33**.

Equipment Code	Estimated Cost (\$)	Quantity	Total cost (\$)
2.E-1	1397200	5	6986000.00
2.P-1	54000	10	540000.00
2.P-2	54000	10	540000.00
2.P-3	27700	10	277000.00
2.P-4	267300	10	2673000.00
2.P-5	25600	10	256000.00
2.T-1	328600	1	5457000.00
2.T-2	328600	1	5457000.00
2.T-3	524500	5	2622500.00
2.T-4	29900	5	149500.00
2.T-5	707100	25	17677500.00
2.V-1	1807300	5	9036500.00
2.V-2	18200	5	91000.00
2.V-3	69800	5	349000.00
Total Equipment Costs			\$ 41,865,200.00

Table 33: Equipment cost summary and total: Growth Reactor

Production/solventogenesis reactor (R2)

Equipment used in the solventogenesis reactor section can be found tabulated in **Table 34**. For the specific nomenclature of the equipment, please refer to **Figure 31**. It should be noted that the listed quantity of each of the item listed covers all of the proposed 5 parallel plant setups, along with the inclusion of all backup systems.

Equipment Code	Equipment Cost (USD/unit)	Qty.	Total equipment cost (USD)
3.V-1	5633500	5	28,167,500.00
3.T-1	328600	1	328,600.00
3.T-2	328600	1	328,600.00
3.T-3	749300	5	3,746,500.00
3.V-2	1300300	1	1,300,300.00
3.T-4	271600	1	271,600.00
3.P-1 (A/B)	115000	10	1,150,000.00
3.P-2 (A/B)	115000	10	1,150,000.00
3.P-3 (A/B)	29800	10	298,000.00
3.P-4 (A/B)	199600	10	1,996,000.00
3.P-5 (A/B)	2091900	10	20,919,000.00
3.P-6 (A/B)	194400	10	1,944,000.00
3.P-7 (A/B)	3600	10	36,000.00
3.E-1 (A/B)	17852000	5	89,260,000.00
3.S-1 (A/B)	-	10	-
Total Equipment Cost			150,896,100.00

Table 34. R2 total equipment cost analysis

Product Work-up

The equipment cost was obtained for all pieces of equipment specified in the equipment lists in **Table 27** through **Table 31**. The corresponding equipment codes can also be found there. The backup pumps are also included in this analysis.

Equipment Code	Estimated Cost (\$)	Quantity	Total cost (\$)
4.C-1	545220	6	3271320
4.C-2	1259973	3	3779919
4.C-3	1354158	1	1354158
4.C-4	648765	1	648765
4.E-1	65052	1	65052
4.E-2	203463	1	203463
4.E-3	772668	6	4636008
4.E-4	73476	6	440856
4.E-5	1242891	3	3728673
4.E-6	81783	3	245349
4.E-7	1936116	1	1936116
4.E-8	885573	1	885573
4.E-9	308295	1	308295
4.E-10	185211	1	185211
4.P-1	13221	6	79326
4.P-2	31941	3	95823
4.P-3	17784	1	17784
4.P-4	36972	1	36972
4.P-5	18720	1	18720
4.P-6	7722	1	7722
4.P-7	17784	1	17784
4.T-1	48672	6	292032
4.T-2	88920	3	266760
4.T-3	104364	1	104364
4.T-4	116883	1	116883
4.T-5	32292	1	32292
Total (1 plant)			22775220
Total (all plants)	22775220	5	113,876,100

Table 35: Equipment cost product work-up

Capital Fixed Investment Costs

To estimate the total investment costs of this process, a scheme to estimate the total investment costs was created using Towler. This is shown in **Table 36**.

Item	Factor (f)
Major equipment cost (C_e)	
Equipment erection	0.3
Piping	0.8
Instrumentation and control	0.3
Electrical	0.2
Civil	0.3
Structures and buildings	0.2
Lagging and paint	0.1
ISBL cost ($C = C_e * (\sum f + 1)$)	$3.2 * C_e$
Offsite cost (OS)	0.3
Design and engineering (DE)	0.3
Contingency (X)	0.1
Total fixed capital costs ($C_{FC} = C(1 + OS)(1 + DE + X)$)	$5.82 * C_e$

Table 36: Investment costs correction factor⁵⁰

Using the total equipment cost of \$ 1,459,032,422.00, the sum of all equipment from each plant section as per appendix 1, the net total capital investment costs was found to be \$ 8,637,472,000.00.

Annual product value

In the current design, approximately 450000 kg/h or 126 kg/s of Ethanol (99.7% purity) is produced, and at a market value of \$ 1.42 per gallon, an annual turnover \$ 1.9 billion is expected.

Ethanol price	1.42	\$/gallon
	0.38	\$/liter
Ethanol produced	454545	kg/h
	576102.6616	l/h
	5050115932	l/year
	\$1,894,420,900.74	\$/year

Table 37: Annual turnover for ethanol product

Conclusion

Converting polluting steel furnace off-gas to ethanol is a very noble idea, and using a bio-reactor to do so even more so, but as illustrated in this report, many challenges stand in the way of an easy off-gas to ethanol fermentation process. As it stands a near \$ 1.9 billion annual turnover is expected from the plant, about 5 million m³ of ethanol. With the annual global production of ethanol at over 80 million metric tons, or near 100 million m³^{5,6}, the plant is set to tap into 5% of global demand, a non-destabilizing output to a very large global demand. The total capital investment cost was derived at \$ 9.0 billion, giving the total plant a roughly 5-year ROI. Despite these seemingly good prospects when one starts to account for annual running costs, the cost of running a plant on this scale becomes clear. The energy consumption of the reactor segment of the plant is roughly 430MW, with an additional 2.7 and 2.8 GW estimated for the syngas cleaning and product work up sections respectively. Using 8.22 euro cents per kW/h quoted in the Netherlands, an estimated \$ 4.99 billion per year would need to be spent on electricity alone to run the plant. The near 5.93 GW consumed by the plant, if located in the Netherlands, would also be roughly 50% of the 12GW of energy the Netherlands consumes⁵⁵. Based on this alone, the plant becomes unprofitable. Note, this doesn't even consider the other operational costs such as water use, and chemicals, or maintenance. Despite the unprofitability of the plant, the current system assumes a near perfect version of the process, where an upscale using microbes relates in a linear, and predictable increase in productivity. With this in mind, the likelihood of a plant existing in the current setup is possibly unlikely, and iterations of bio-fermentation to syngas plants will need to implement more economical processes to make such a process viable. A foreseeable design would need to omit a syngas cleaning operation to cut the huge costs of syngas cleanup. This would result in a system with very little syngas pretreatment, but much better prospects at becoming profitable, since the syngas pretreatment segment in this design consumes the most energy, and is responsible for 85% of the initial capital investment.

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Appendix

1) Equipment costs list

Equipment Code	Estimated Cost (\$)	Quantitiy	Total cost (\$)
1.E-1	2282400	4	9129600
1.E-2	14681800	13	190863400
1.E-3	14289600	24	342950400
1.E-4	1013700	1	1013700
1.E-5	8578500	1	8578500
1.E-6	674000	5	3370000
1.K-1	66379798,86	7	464658592
1.K-2	66379800	1	66379800
1.K-3	1057700	1	1057700
1.P-1/P-2/P-3	16850	21	353850
1.S-1	14000	500	7000000
1.S-2	155000	1	155000
1.S-3	1203	4000	4812000
1.V-1	4277300	4	17109200
1.V-2a/b	1555000	50	77750000
1.V-3	464700	30	13941000
1.V-4	205640	5	1028200
1.V-5	205640	4	822560
1.T-1	2704600	1	2704600
1.T-2	9785500	2	19571000
2.00E-01	1397200	5	6986000
2.P-1	54000	10	540000
2.P-2	54000	10	540000
2.P-3	27700	10	277000
2.P-4	267300	10	2673000
2.P-5	25600	10	256000
2.T-1	328600	1	5457000
2.T-2	328600	1	5457000
2.T-3	524500	5	2622500
2.T-4	29900	5	149500
2.T-5	707100	25	17677500
2.V-1	1807300	5	9036500

2.V-2	18200	5	91000
2.V-3	69800	5	349000
3.V-1	5633500	5	28167500
3.T-1	328600	1	328600
3.T-2	328600	1	328600
3.T-3	749300	5	3746500
3.V-2	1300300	1	1300300
3.T-4	271600	1	271600
3.P-1 (A/B)	115000	10	1150000
3.P-2 (A/B)	115000	10	1150000
3.P-3 (A/B)	29800	10	298000
3.P-4 (A/B)	199600	10	1996000
3.P-5 (A/B)	2091900	10	20919000
3.P-6 (A/B)	194400	10	1944000
3.P-7 (A/B)	3600	10	36000
3.E-1 (A/B)	17852000	5	89260000
3.S-1 (A/B)		10	
4.C-1	545220	6	3271320
4.C-2	1259973	3	3779919
4.C-3	1354158	1	1354158
4.C-4	648765	1	648765
4.E-1	65052	1	65052
4.E-2	203463	1	203463
4.E-3	772668	6	4636008
4.E-4	73476	6	440856
4.E-5	1242891	3	3728673
4.E-6	81783	3	245349
4.E-7	1936116	1	1936116
4.E-8	885573	1	885573
4.E-9	308295	1	308295
4.E-10	185211	1	185211
4.P-1	13221	6	79326
4.P-2	31941	3	95823
4.P-3	17784	1	17784
4.P-4	36972	1	36972
4.P-5	18720	1	18720
4.P-6	7722	1	7722
4.P-7	17784	1	17784
4.T-1	48672	6	292032
4.T-2	88920	3	266760
4.T-3	104364	1	104364
4.T-4	116883	1	116883
4.T-5	32292	1	32292
Total			\$ 1.459.032.422,00

2) Equipment Specifications list

Equip ment Code	Title	Capac ity (m3) V (m3/h)	Press ure (bar)	Temper ature (OC)	Duty (kW)	MoC	Dimension s	Comme nt
1.E-1	Heat exchang er (Shell and tube)	7.00E +05	10	Hot fluid outlet: 20°C	39258 5	Tube: 316LW, Shell: 316L	7160.72 m2	
1.E-2	Heat exchang er (Shell and tube)	1.10E +06	1	Hot fluid outlet: 37-50 °C	75043 4	Tube: 316LW, Shell: 316L	46275 m2	
1.E-3	Heat exchang er (Shell and tube)	2.00E +06	1	Hot fluid outlet: 650-760 °C	98495 6	Tube: 316LW, Shell: 316L	45050.2 m2	
1.E-4	Furnace	1.00E +06	10	Gas outlet: 1500- 1800 °C	10394 99	SS 316, Insulation: Ceramic foam (Al2O3)	-	
1.E-5	Heat exchang er (Shell and tube)	8.00E +05	10	Hot fluid outlet: 40 °C	44325 2	Tube: 316LW, Shell: 316L	27060 m2	
1.E-6	Heat exchang er (Shell and tube)	3.30E +05	10	Hot fluid outlet: 37 °C	21971	Tube: 316LW, Shell: 316L	2076 m2	
1.K-1	Compres sor	5,00E +05	10	20 °C	39922 85	SS 316	-	
1.K-2	Compres sor	5,00E +05	10	37-50 °C	43778 7	SS 316	-	
1.K-3	Compres sor	2562	20	-	758	SS 316	-	

1.P-1/P-2/P-3	Positive displacement pump	100	dP=0	20 °C	-	SS 316/Carpenter 20/Carpenter 20	-	
1.S-1	Cyclone	1.2 Mton/year syngas	1	20 °C	-	SS	r = 0.25, H = 1 [C]	
1.S-2	Demister	3.54E+06	1	37-50 °C	-	SS 316	-	
1.S-3	Nitrogen membrane filter	198	10	37-50 °C	-	SS 316	1.625*0.812*2.286	
1.V-1	Tar reformer	2.70E+06	10	1500-1800 °C	266715	SS 316, Insulation: Ceramic foam (Al2O3)	r = 5.0, H = 50 [C]	
1.V-2a/b	Fixed bed reactor a/b	60 kmol/h H2S	10	650-760 °C	2713/10088	316L	r = 0.875, H = 4.5 [C]	
1.V-3	CSTR	108 kmol/h (NO+SO2)	1	37-50 °C	-690	Monel	r = 1.75, H = 8.0 [C]	
1.V-4	Nitrogen storage vessel	500	20	20 °C	-	SS 316	r = 4.0, H = 10 [C]	
1.V-5	SO2 neutralization vessel	500	1	20 °C	-	SS 316	r = 4.0, H = 10 [C]	
1.T-1	0.2M KMnO4 solution storage tank	500 (0.2M)	1	20 °C	-	SS 316	r = 1.25, H = 25 [C]	
1.T-2	2M NaOH solution storage tank	500 (2M)	1	20 °C	-	Monel	r = 1.25, H = 25 [C]	
2.00E-01	Internal cooling Coil - Growth Reactor	1400	1	18-37	30700	SS316L	A = 1800 m2	Area refers to surface area of bare coil needed. Positive displacement pump
2.P-1	Acid Pump	72	1-10, dp=9	25		SS316	-	

2.P-2	Base Pump	72	1-10, dp=9	25		SS314	-	Positive displacement pump
2.P-3	Nutrient Stock Pump	62	1-10, dp=9	25		SS304	-	
2.P-4	Water Pump (Growth Reactor)	1000	1-10, dp=9	25		SS304	-	
2.P-5	2.V-1 Medium pump	1030	10, desired dp = 0	37		SS304	-	Pumping Medium from Growth to Production Reactor
2.S-1[i]	Syngas org-material filter x 50	6700	10	37	-	Polytetrafluoroethylene membrane	$r = 0.07, H = 0.25 [C]$	(Area per filter = $0.88m^2$) Total area = $44m^2$
2.T-1	2M HCl storage	806	1	25	-	SS904L	$r = 4.41, H = 13.21 [C]$	
2.T-2	2M HCl storage	806	1	25	-	SS904L	$r = 4.41, H = 13.21 [C]$	
2.T-3	Nutrient Storage tank.	1700	1	25	-	SS304	$r = 7.81, H = 8.85 [C]$	@ max Vol. capacity leaves 1 m head (only needs 1700)
							$r = 1.5, h = 1.62$	@max Vol. leaves 0.15m head space. (only needs 10m3)
2.T-4	Antifoam 204 tank	11	1	25	-	SS304	[C]	@max Vol. leaves 0.75m head space (only need 2500x5 - total capacity = $12500m^3$)
							$r = 9.3, H = 10.0$	@ max leaves 1.8m head room (needs 830m3)
2.T-5	Water reservoir (x 5)	2500	1	25	-	SS304	[C]	
2.V-1	Growth Reactor (stirred)	900	10	37	-	SS304	$r = 3.54, H = 23 [DC]$	

2.V-2	Non cooled flasher/Pressure changer	Volum e = 0.9 Flow = 3150	10-1, dp = - 9	20	144.8	SS304	r = 0.3, H = 3 [DC]	Used Souders Formula
2.V-3	Cooled Flasher/ 1 bar	Volum e = 31, Flow = 66500	1	10	340.4	SS304	r = 1.2, H = 6 [DC]	Used Souders Formula
3.V-1	Reaction pressure vessel	3500	10	35	-	Stainless steel (SS304)	D=9.053, H=54.32 [DC]	Operating pH=4.4-4.8; used for microbe catalyzed fermentation
3.T-1	Storage vessel	806	1	25	-	Stainless steel (SS904L)	D=8.808, H=13.21 [C]	Operating pH=14; used for containment of aqueous NaOH 2M solution
3.T-2	Storage vessel	806	1	25	-	Stainless steel (SS904L)	D=8.808, H=13.21 [C]	Operating pH=0.3; used for containment of aqueous HCl 2M solution
3.T-3	Storage vessel	3500	1	35	-	Stainless steel (SS304)	D=14.37, H=21.55 [C]	Operating pH=4.4-4.8; used for containment of 3.V-1 liquid outlet stream

3.V-2	Flasher vessel	500	10	35	-	Stainless steel (SS304)	D=7.512, H=11.27 [C]	Operating pH=4.4-4.8; used for 3.V-1 liquid outlet stream pressure relief from 10 bar to 1 bar (atmospheric)
3.T-4	Storage vessel	806	1	25	-	Stainless steel (SS904L)	D=8.808, H=13.21 [C]	Operating pH=7; used for containment of water
3.P-1 (A/B)	Base positive displacement dosing pump	Variable	1-10, dp=9	25	-	Stainless steel (SS904L)	-	Operating pH=14; used for transport of aqueous NaOH 2M solution
3.P-2 (A/B)	Acid positive displacement dosing pump	Variable	1-10, dp=9	25	-	Stainless steel (SS904L)	-	Operating pH=0.3; used for transport of aqueous HCl 2M solution
3.P-3 (A/B)	Liquid single stage centrifugal pump	1200	-	35	-	Stainless steel (SS304)	-	Operating pH=4.4-4.8; used for transport of 3.V-1 liquid

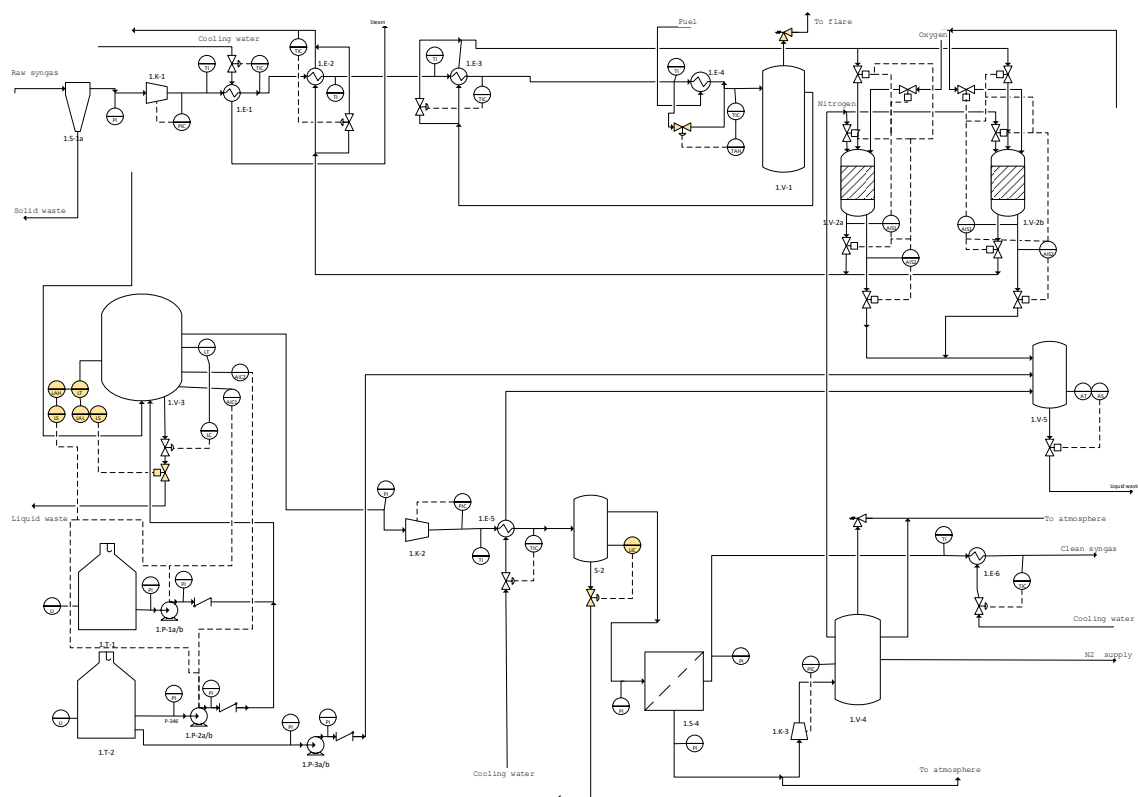
								outlet stream
3.P-4 (A/B)	Gas single stage centrifugal pump	5000	-	35	-	Stainless steel (SS304)	-	Used for inlet gas transport to 3.V-1
3.P-5 (A/B)	Gas reciprocating positive displacement dosing pump	17500	-	35	-	Stainless steel (SS304)	-	Used for gaseous H ₂ gas transport to 3.V-1
3.P-6 (A/B)	Water positive displacement dosing pump	Variable	1-10, dp=9	25	-	Stainless steel (SS304)	-	Operating pH=7; used for transport of water in case of emergency
3.P-7 (A/B)	Antifoam positive displacement dosing pump	Variable	1-10, dp=9	25	-	Stainless steel (SS304)	-	Used for transport of antifoam 204
3.E-1 (A/B)	Internal cooling coil	-	10	35	400000	Stainless steel (SS304)	-	Dimensions and cost of this equipment follows and is included in 3.V-1; used for temperature control of 3.V-1

3.S-1 (A/B)	Hollow fiber membrane filter module	650	-	35	-	Polysulfone	-	130 individual filter per module; pH=4.4- 4.88; Pore size=0.4 μm; used for solid- liquid separation of 3.V-1 liquid outlet stream
4.C-1	Distillation column	187	1	80-100	-	SS304	D = 3.88, H = 12.8	
4.C-2	Distillation column	90	1	70-100	-	SS304	D = 3.99, H = 23.0	
4.C-3	Extractive distillation column	130	1-3.5	70-200	-	SS304	D = 3.00, H = 26	
4.C-4	Solvent recovery column	114	1	100-200	-	SS304	D = 3.89, H = 11	
4.00E-01	First feed pre-heater	105/11 27	1	20-200	40536	SS304	A = 169	Shell and tube
4.00E-02	Second feed pre-heater	1127	1	26-60	8969	SS304	A = 737	Shell and tube
4.00E-03	Column 1 condenser	45	1	81	37387	304LW	A = 1226	Air cooler
4.00E-04	Column 1 reboiler	79	1	100	45279	SS304	A = 121	Kettle reboiler
4.00E-05	Column 2 condenser	217	1	72	53808	304LW	A = 2070	Air cooler
4.00E-06	Column 2 reboiler	95	1	100	54737	SS304	A = 146	Kettle reboiler
4.00E-07	Column 3 condenser	368	1	73	88415	304LW	A = 3336	Air cooler
4.00E-08	Column 3 reboiler	227	1	193	98207	SS304	A = 2297	Kettle reboiler
4.00E-09	Column 4 condenser	18	1	99	14917	304LW	A = 472	Air cooler

4.00E-10	Column 4 reboiler	63	1	197	14402	SS304	A = 362	Kettle reboiler
4.P-1a/b	Column 1 condenser pump	45	1	81	-	SS304	-	Centrifugal pump
4.P-2a/b	Column 2 condenser pump	217	1	72	-	SS304	-	Centrifugal pump
4.P-3a/b	Solvent pump	94	1	20	-	SS304	-	Centrifugal pump
4.P-4a/b	Column 3 condenser pump	368	1	73	-	SS304	-	Centrifugal pump
4.P-5a/b	Column 4 feed pump	114	1	193	-	SS304	-	Centrifugal pump
4.P-6a/b	Column 4 condenser pump	18	1	99	-	SS304	-	Centrifugal pump
4.P-7a/b	Solvent recycle pump	94	1	197	-	SS304	-	Centrifugal pump
4.T-1	Column 1 reflux drum	7,5	1	81	-	SS304	D = 1.5, L = 4.24	Horizontal drum
4.T-2	Column 2 reflux drum	36	1	72	-	SS304	D = 2.5, L = 7.33	Horizontal drum
4.T-3	Solvent tank	100	1	20	-	SS304	D = 4.5, H = 6.29	Vertical storage tank
4.T-4	Column 3 reflux drum	61	1	73	-	SS304	D = 3, L = 8.63	Horizontal drum
4.T-5	Column 4 reflux drum	3	1	99	-	SS304	D = 1.2, L = 2.65	Horizontal drum

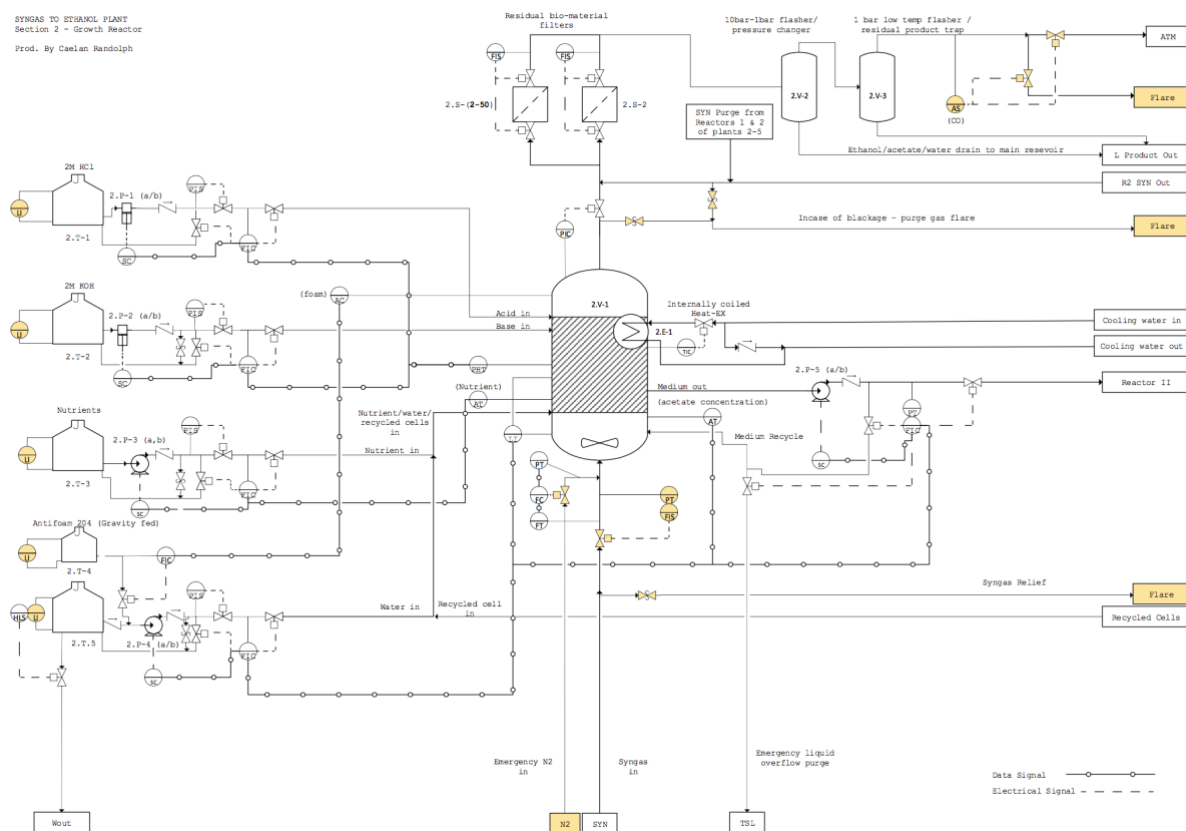
3) P&ID

Syngas cleanup

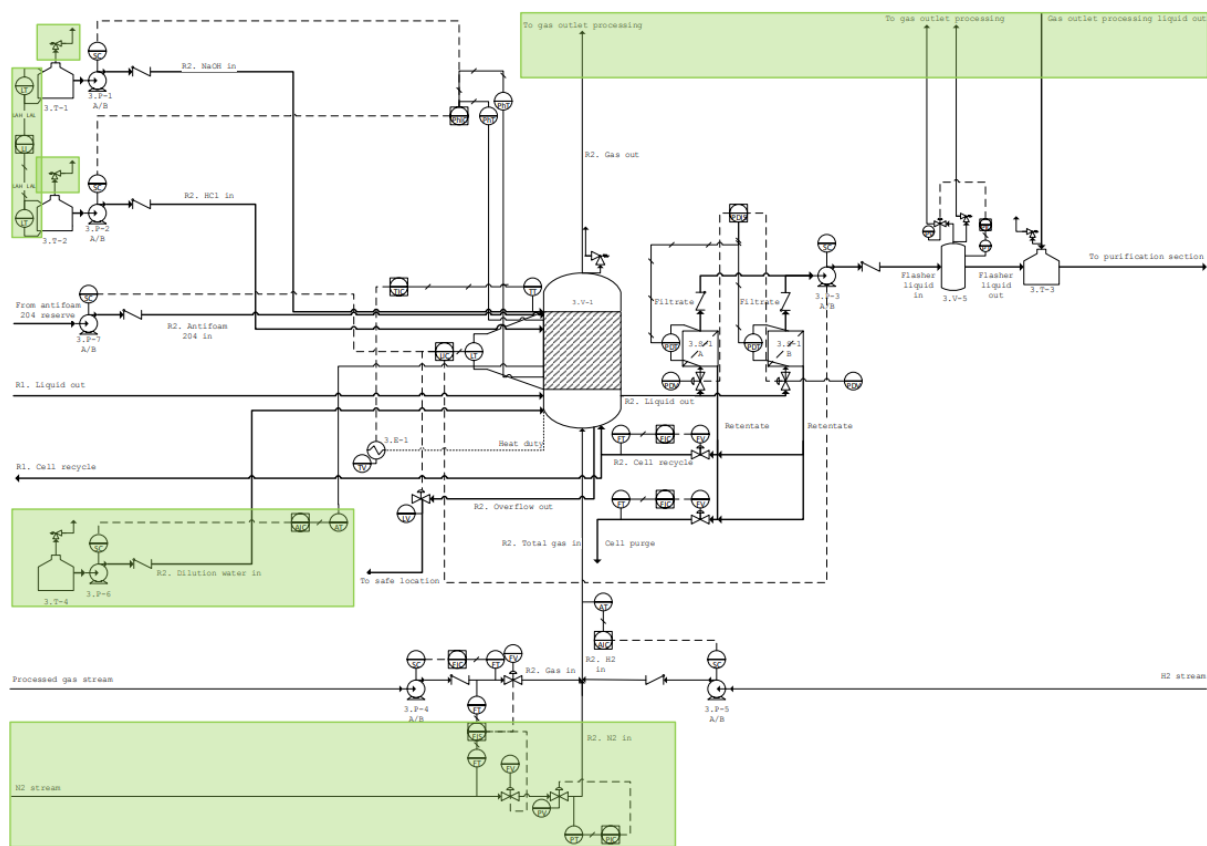


Growth Reactor

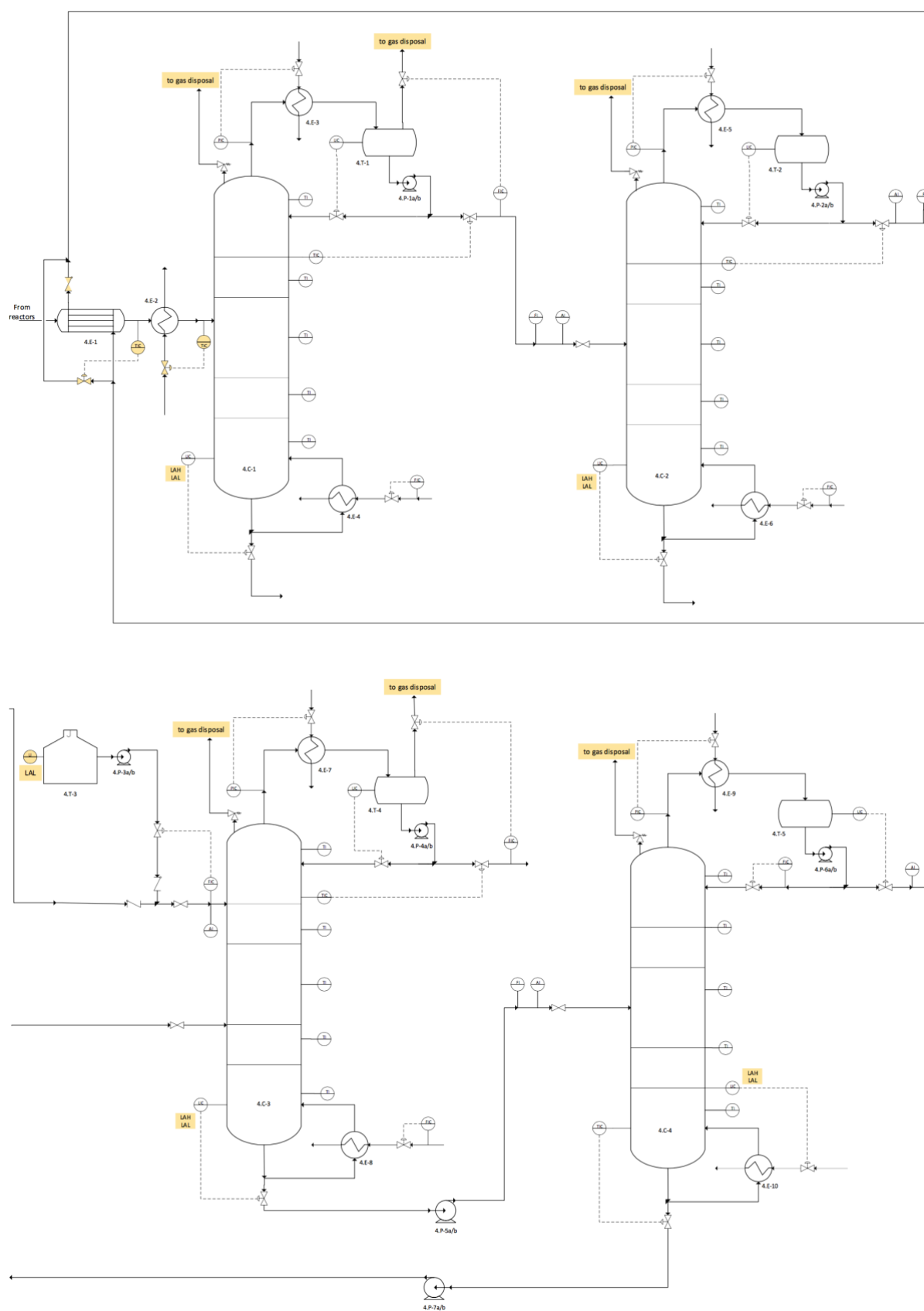
SYNGAS TO ETHANOL PLANT
Section 2 - Growth Reactor
Prod. By Caslan Randolph



Production Reactor

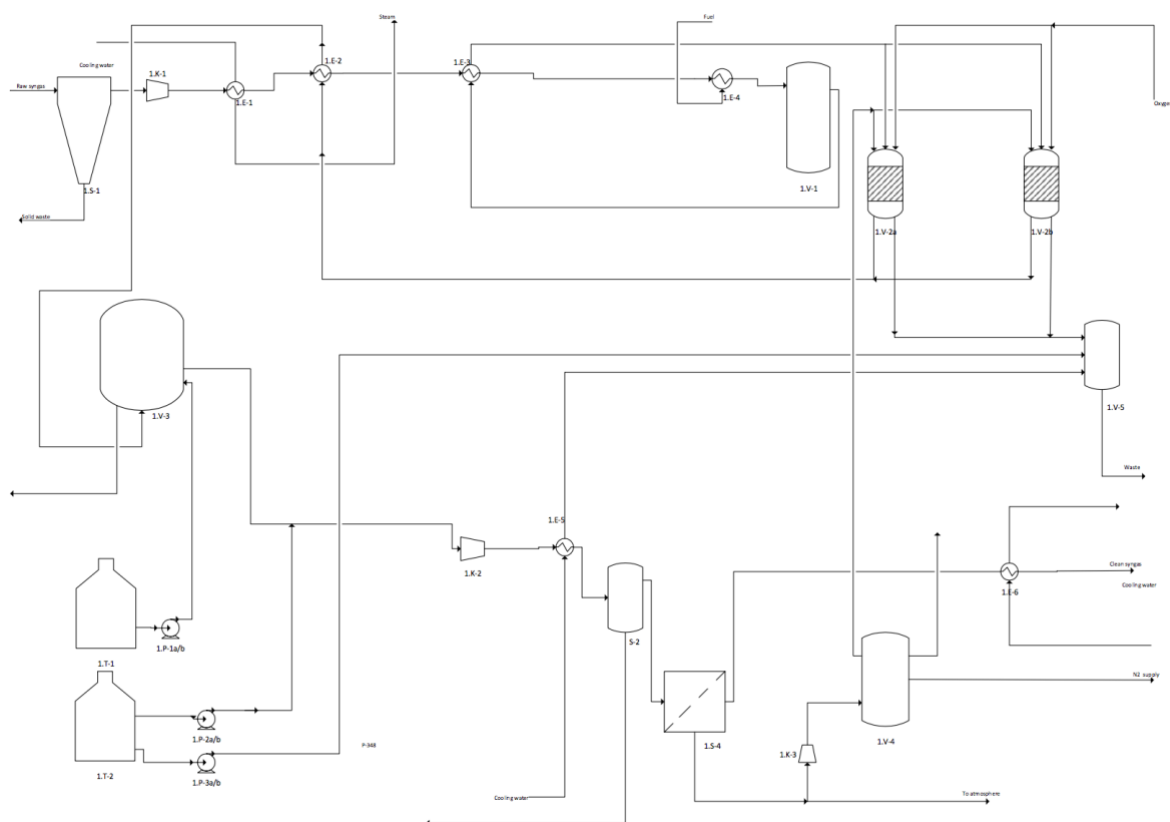


Product work-up



4) PFD

Syngas Processing



Remaining reactor and product processing

